Phase Transfer Catalyzed Synthesis of Organosulfur Fine Chemicals using Hydrogen Sulfide

Gaurav Singh

Department of Chemical Engineering
National Institute of Technology, Rourkela

Phase Transfer Catalyzed Synthesis of Organosulfur Fine Chemicals using Hydrogen Sulfide

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Gaurav Singh

(Roll Number: 512CH103)

under the supervision of

Prof. Sujit Sen

Department of Chemical Engineering
National Institute of Technology Rourkela

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Department of Chemical Engineering
National Institute of Technology Rourkela

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Certificate of Examination

Roll Number: 512CH103

Name: Gaurav Singh

Title of Dissertation: Phase Transfer Catalyzed Synthesis of Organosulfur Fine Chemicals using Hydrogen Sulfide

We, the below signed, after checking the dissertation mentioned above and the official record book (s) of the student, hereby state our approval of the dissertation submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy in Chemical Engineering at National Institute of Technology Rourkela. We are satisfied with the volume, quality, correctness, and originality of the work.

Sujit Sen
Supervisor

Saurav Chatterjee
Member (DSC)

Madhusree Kundu
Member (DSC)

Pradip Chowdhury
Member (DSC)

HOD, Chemical Engineering
Chairman (DSC)

Anand V. Patwardhan
Examiner

Department of Chemical Engineering
National Institute of Technology Rourkela

Dr. Sujit Sen
Assistant Professor

June 17, 2016

Supervisor's Certificate

This is to certify that the work presented in this dissertation entitled **''Phase Transfer Catalyzed Synthesis of Organosulfur Fine Chemicals using Hydrogen Sulfide**" by "Gaurav Singh", Roll Number 512CH103, is a record of original research carried out by him under my supervision and guidance in partial fulfillment of the requirements of the degree of *Doctor of Philosophy* in *Chemical Engineering*. Neither this dissertation nor any part of it has been submitted for any degree or diploma to any institute or university in India or abroad.

Sujit Sen

Dedicated to My Mother

Declaration of Originality

I, Gaurav Singh, Roll Number 512CH103, hereby declare that this dissertation entitled "Phase Transfer Catalyzed Synthesis of Organosulfur Fine Chemicals using Hydrogen Sulfide" represents my original work carried out as a doctoral student of NIT Rourkela and, to the best of my knowledge, it contains no material previously published or written by another person, nor any material presented for the award of any other degree or diploma of NIT Rourkela or any other institution. Any contribution made to this research by others, with whom I have worked at NIT Rourkela or elsewhere, is explicitly acknowledged in the dissertation. Works of other authors cited in this dissertation have been duly acknowledged under the section "Bibliography". I have also submitted my original research records to the scrutiny committee for evaluation of my dissertation.

I am fully aware that in case of any non-compliance detected in future, the Senate of NIT Rourkela may withdraw the degree awarded to me on the basis of the present dissertation.

June 17, 2016 Gaurav Singh

NIT Rourkela

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Abstract

The focus of this study is to utilize hydrogen sulfide (H_2S) in the synthesis of fine chemicals, such as, thioethers and organic disulfides. Two different aqueous alkanolamines, such as, N-methyldiethanolamine (MDEA) and monoethanolamine (MEA) were used for the absorption H_2S to make H_2S-rich alkanolamine solution. Dibenzyl sulfide (DBS) and dibenzyl disulfide (DBDS) were synthesized from the reaction of H_2S-rich alkanolamine with organic reactant, benzyl chloride (BC). To carry out this biphasic reaction, three different phase transfer catalysts (PTCs) were used, namely, tetrabutylphosphonium bromide (TBPB), trihexyl(tetradecyl)phosphonium chloride (THTDPC) an ionic liquid (ILs) and a solid catalyst, amberlite IR-400. The main objective of the present study is to utilize H_2S in synthesizing value-added chemicals such as DBS and DBDS, along with maximization of the conversion of the organic reactant, and the selectivity of desired product. Three different reaction systems have been carried out for the present work. First system dealt with the synthesis of DBS from the reaction of H_2S-rich MDEA and BC using TBPB as PTC under liquid-liquid (L-L) phase transfer catalysis (PTC). Parametric study, mechanistic investigation and kinetic modeling have been performed for this system. In the second system, DBS was synthesized using THTDPC as a PTC under L-L PTC condition with around 98% BC conversion and 100% DBS selectivity. Parametric study and mechanistic investigation was performed and a detailed kinetic model was developed and validated using experimental values. In the last system, an investigation has been done on the utilization of H_2S for the synthesis of DBDS under liquid-liquid-solid (L-L-S) PTC using amberlite IR-400 as a solid PTC. The effect of different parameters on the BC conversion was studied and the selectivity of desired product DBDS was found to be 100% at some level of process parameters. A suitable reaction mechanism has been proposed and a mathematical model has been developed and validated to explain the kinetics of the reaction.

Keywords: Hydrogen sulfide; dibenzyl sulfide; dibenzyl disulfide; methyldiethanolamine; monoethanolamine; phase transfer catalyst; selectivity; kinetic modeling.

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Nomenclature

S^{2-}	Sulfide anion
S_2^{2-}	Disulfide anion
Q^+	Catalyst cation
QSQ	Catalyst active intermediate
QSH	Catalyst active intermediate
Q_2S_2	Catalyst active intermediate
C_r	Concentration of the reactant
C_s	Concentration of Sulfide
C_c	Concentration of catalyst
C_{r0}	Initial concentration of reactant
C_{s0}	Initial concentration of sulfide
f	Ratio of the volume of the organic phase to that of aqueous phase
k_{app}	Apparent rate constant
$(-r_A)_{pred}$	Predicted rate of reaction
$(-r_A)_{expt}$	Experimental rate of reaction
K_{R_3N}	Dissociation constant for MDEA
K_{H_2S}	Dissociation constant for hydrogen sulfide
K_{HS^-}	Dissociation constant for hydrosulfide anion
K_{H_2O}	Dissociation constant for water
T_{R_3N}	Total concentration of MDEA
T_S	Total sulfide concentration
$[S^{2-}]$	Concentration of sulfide anion
$[S_2^{2-}]$	Concentration of disulfide anion
$[HS^-]$	Concentration of hydrosulfide anion
$[H_2S]$	Concentration of hydrogen sulfide
$[R_3N]$	Concentration of MDEA

$[Q^+Cl^-]_{aq}$	Catalyst concentration in aqueous phase
$[Q^+Cl^-]_{org}$	Catalyst concentration in organic phase
$[Q^+HS^-]_{aq}$	Concentration of active site in aqueous phase
$[Q^+HS^-]_{org}$	Concentration of active site in organic phase
$[Cl^-]_{aq}$	Concentration of chlorine anion in aqueous phase
$[Q^+]_{tot}$	Total concentration of catalyst
K_e	Selectivity equilibrium constant
K_{QCl}	Distribution constant of catalyst
K_{QHS}	Distribution constant of active site
$[RCL]_{org}$	Concentration of organic substrate in organic phase
$[RCL]_{org}$	Initial concentration of organic substrate
k_{org}	Overall reaction rate constant
V_{org}	Total volume of organic phase
$\emptyset$	Fraction of the catalyst cation Q^+ distributed in the organic phase
N_Q	Total amount of the catalyst
$[N_Q]_{org}$	Total concentration of the catalyst in organic phase
X_{RCl}	Fractional conversion of organic reactant
K_S	Equilibrium attachment/detachment constants for S_2^{2-}
K_{Cl}	Equilibrium attachment/detachment constants for Cl^-
θ_S	Fractions of the total number of triphase catalyst cation attached to S_2^{2-}
θ_{Cl}	Fractions of the total number of triphase catalyst cation attached to Cl^-
θ_{ClS}	Fractions of the total number of triphase catalyst cations attached to both S_2^{2-} and Cl^-
T	Time

Abbreviation

BM	Benzyl mercaptan
DBS	Dibenzyl sulfide
DBDS	Dibenzyl disulfide
DEA	Diethylamine
DGA	Diglycolamine
DIPA	Diisopropylamine
H_2S	Hydrogen sulfide
ILs	Ionic liquids
IPTC	Inverse phase transfer catalysis
L-L PTC	Liquid-liquid phase transfer catalysis
L-L-S PTC	Liquid-liquid-solid phase transfer catalysis
MEA	Monoethanolamine
MDEA	Methyldiethanolamine
PEG	Polyethylene glycole
PTC	Phase transfer catalyst
RPTC	Reverse phase transfer catalysis
TBPB	Tetrabutylphosphonium bromide
TBAB	Tetrabutylammonium bromide
TBAI	Tetrabutylammonium iodide
TBAC	Tetrabutylammonium chloride
TBAOH	Tetrabutylammonium hydroxide
TBAA	Tetrabutylammonium acetate
TBGA	N-tertiarybutyl diethylene glycolamine
THTDPC	Trihexyl(tetradecyl)phosphonium chloride (THTDPC)
THTDPB	Trihexyl(tetradecyl)phosphonium bromide
THTDPD	Trihexyl(tetradecyl)phosphoniumdecanoate
THTDPH	Trihexyl(tetradecyl)phosphoniumhexafluorophosphate

Chapter 1

Introduction

This chapter gives an account of the sources of emission of hydrogen sulfide (H_2S), necessity for the removal of the gas, present industrial processes for the removal, and utilization of the gas, objective of the work and organization of the thesis.

1. INTRODUCTION

1.1 Environmental emission of hydrogen sulfide

Hydrogen sulfide (H_2S; CAS No. 7783-06-4) is a flammable hazardous colourless gas with a characteristic rotten egg odour (Lindenmann et al., 2010). H_2S occurs naturally in crude petroleum, natural gas, volcanic gases and hot springs. 90% of the total H_2S emission in the atmosphere is due to natural sources (US EPA, 1993). H_2S is formed naturally via reduction of organosulfur compounds by micro-organism (Hill, 1973).

Build-up of H_2S in the atmosphere is because of a variety of industrial operations such as petroleum refineries, natural gas plants, petrochemical plants, Kraft paper mills, iron smelters, coke oven plants, food processing plants, and tanneries.

Refineries these days are compelled to treat heavy-crudes that contain lots of organosulfur compounds. To reduce the concentration of sulfide up to the recommended level set by environmental protection agencies, typical desulfurization process is used which converts those organosulfur compounds into hydrogen sulfide (H_2S). Reclamation of sulfur is an essential part of these large processes where about 5 kg of H_2S may be formed from 300 litres of a high sulfur crude.

In some cases, natural gas may contain as high as 50% H_2S which must be removed before vending for heating and power generation.

Kraft mills are another large potential source of H_2S. H_2S is produced during each step of the Kraft process. H_2S is recovered by allowing it to react with Na_2CO_3, or $NaHCO_3$, in the presence of oxygen to yield Na_2SO_4, and Na_2SO_4.

Coke ovens produces as much as 10 ppm of H_2S by burning coal. Scrubbing of coke oven gas can remove around 50% of the H_2S. Complete removal of H_2S is being performed before circulation as a municipal gas.

1.2 Necessity of H_2S removal

H_2S is categorised as a very harmful industrial waste. It is very poisonous at low concentration. It is corrosive in presence of water and becomes flammable in presence of air (Beauchamp et al. 1984; Legator et al. 2001; Lindenmann et al., 2010; Reiffenstein et al. 1992; Syed et al. 2006). The removal of H_2S from by-product gas streams is very essential because the reasons depicted below:

- H_2S is a highly noxious gas, and very pungent. Prescribed level of H_2S in industries should be between 0.5-10 ppm. It can become deadly when it leakages out and builds up at the work place.

- H_2S is very eroding in aqueous environment, so it must be eliminated completely from the gas streams ahead of further handling and transportation through pipelines. (Dillon, 1990).

- Deactivation of catalysts in downstream processes as well as corrosion of the process equipment may occur if the concentration of H_2S would not bring down below the prescribed limit. (Hamblin, 1973).

Industrial workers are largely exposed to H_2S by breathing it. The health effects depend on how much H_2S they breathe and for how long. Exposure to very high concentrations can also quickly lead to death. Acute symptoms and effects due to inhaling of the gas are shown below:

Table 1.1 Health effect at various exposure level of H_2S (OSHA standards; Lindenmann et al., 2010)

Concentration (ppm)	Symptoms/Effects
0.00011-0.00033	Typical background concentrations
0.01-1.5	Odour threshold.
2-5	Nausea, loss of sleep, headache weight loss, diarrhoea
50-100	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
100	Mild eye and lung irritation, coughing, sore throat, altered breathing, drowsiness.
100-150	Loss of smell (olfactory fatigue or paralysis)
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur from prolonged exposure
500-700	Staggering, collapse in 5 minutes, damage to the eyes in 30 minutes, death after 30-60 minutes
700-1000	Rapid unconsciousness, death within 5 minutes
1000	Nearly instant death

1.3 Industrial processes for H_2S removal and recovery

Due to severe environmental and health problems mentioned in above section the H_2S concentration in the tail gas streams need to be cut down to the safe limit before further handling. H_2S can be removed by either of the six different processes –

- Absorption in alkaline solution
- Physisorption in glycols/ethers
- Absorptive oxidation
- Dry sorption/reaction
- Membrane permeation
- Adsorption.

For treatment of high-volume gas streams containing H_2S (and/or carbon-di-oxide), both chemisorption in alkaline media (e.g., aqueous alkanolamines) and physisorption in a physical solvent (e.g., polyethylene glycol, dimethyl ether) are appropriate process techniques. However, physisorption processes are not economical when the acid gas partial pressure is low because the capacity of physical solvents is a strong function partial pressure. Since the present research focuses on synthesis of valuable fine chemicals using H_2S, the discussion on removal of H_2S is restricted on only the chemisorption by alkanolamine solutions, which will produce aqueous sulfide necessary for synthesis of organosulfur fine chemicals.

When H_2S is absorbed in aqueous alkaline solutions or physical solvents, they are typically regenerated without experiencing a chemical change. If the regenerated off-gas comprises of more than 10 tons/day of H_2S, it is generally suggested to transform the H_2S to elemental sulfur in a conventional Claus-type processes. For smaller concentration of H_2S in tail gas, direct oxidation may be the desired route. Direct oxidation can be performed by absorption in a liquid followed by oxidation to form solid sulfur slurry or sorption on a solid with or without oxidation. The solid sorption routes are mainly appropriate for very small amounts of gas where working simplicity is important. Solid sorption routes can also be applied to treat high-temperature gas streams, which cannot be treated by conventional liquid absorption methods.

Adsorption is a feasible option for gases containing small concentration of H_2S and heavier sulfur compounds such as mercaptans and carbon disulfide. There are various well-developed and industrially acceptable methods for H_2S removal as discussed below.

1.3.1 Ammonia-based process

The use of NH_3 to remove H_2S from tail gas streams has dropped in recent years. However, the method is still utilized to desulfurize coke-oven gas in a few installations. ammonia-based H_2S treatment processes are undertaken by the Davy-Still Otto (1992), Krupp Wilputte Corporation (1988), and Mitsubishi Kakoki Kaisha, Ltd. (Fumio, 1986).

The reactions taking place in the ammonia-based H_2S treatment processes can be represented as follows:

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

$$NH_3 + H_2S \rightleftharpoons NH_4HS$$

$$2\ NH_3 + H_2S \rightleftharpoons (NH_4)_2S$$

Scheme 1.1. Hydrogen sulfide in aqueous ammonia

Ionic ammonium ion (NH^{4+}), as well as undissociated NH_3, are both present in aqueous solution under equilibrium conditions in measurable quantities (Van Krevelen, 1949). In aqueous ammonia, H_2S is mostly present in the form of HS^- ions.

NH_3-based processes are no longer of industrial importance because of the following reasons:

- High partial pressure of NH_3 in aqueous ammonia solution leads to vapour loss, enhances the complexity and economics of the process.
- Cumbersome regeneration of the rich absorbent is a problematic area in NH_3-based processes because of the formation of heat-stable salts.

1.3.2 Alkanolamine-based processes

Bottoms (1930) patented many technologies for the development of alkanolamines as absorbents for removal acidic gases. In the early gas treatment plants, Triethanolamine (TEA)-based processes was the first commercially available alkanolamine-based process. Slowly other members of the alkanolamines family were brought into the market as a potential acid-gas absorbent. Adequate data are now available on numerous alkanolamines to support design engineers to decide on the most appropriate compound for each specific requirement.

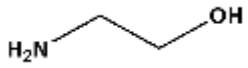
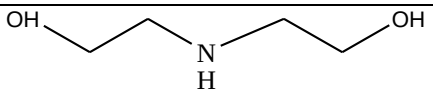
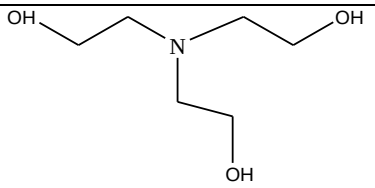
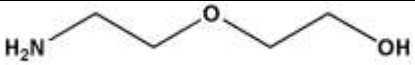
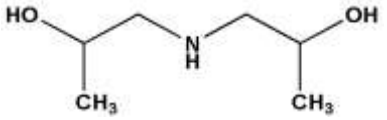
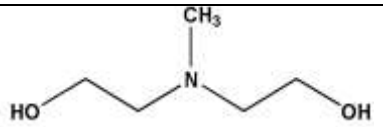
Alkanolaine-based processes are improved processes for H_2S removal. Plenty of work has already been performed and published on H_2S removal using alkanolamine based processes (Al-Baghli et al. 2001; Austgen et al. 1991; Haghtalab et al. 2014; Isaacs et al. 1980; Mandal et al. 2005; Murrieta-Guevara et al. 1992; Sadegh et al. 2015). In this process, the sour gasses containing H_2S and CO_2 or both are allowed to pass through the amine gas treating plant which includes an absorber and a regenerator unit with it. When the gasses containing H_2S contacted counter-currently the down flowing amine solution, they absorb H_2S and CO_2 and the gasses become sweetened. The rich amine further

passes through the regenerator which regenerates the amine for further recycling in the absorber. A typical amine treatment unit is shown in Fig. 1.8.

The alkanolamines that have ascertained to be of foremost commercial interest for acid gas treatment are monoethanolamine (MEA), diethanolamine (DEA), Diisopropanolamine (DIPA), 2-(2-aminoethoxy) ethanol (DGA) and methyldiethanolamine (MDEA). The main advantages and disadvantages of these alkanolamines are presented in Table 1.5. Low reactivity (as a tertiary amine), low absorbing capacity (resulting from higher equivalent weight), and its comparatively poor stability resulted in replacement of triethanolamine (TEA) by other alkanolamines. Diisopropanolamine (DIPA) (Bally, 1961; Klein, 1970) is being employed to some degree in the Adip process, Sulfinol process, and SCOT process for Claus plant tail gas cleansing. Nevertheless, MDEA has slowly replaced DIPA as selective H_2S absorber. The use of MDEA in industrial processes has only become important in recent years. 2-(2-aminoethoxy) ethanol, commercially branded as diglycolamine (DGA), can be used in more concentrated solutions than MEA as it combines the stability and reactivity of MEA with the low vapour pressure and hydroscopicity of diethylene glycol (Kohl, 1997).

Chemical structure of the industrially used important alkanolamines are portrayed in Table 1.2**.** Each has at least one amino group and one hydroxyl group. The beauty of alkanolamines lies in the fact that the amino group offers the essential alkalinity in water solutions to effect the absorption of H_2S and the hydroxyl group helps to lessen the vapor pressure and increase the water solubility.

Table 1.2 Different alkanolamines used for H_2S removal

Alkanolamines	Structure
Monoethanomamine (MEA)	
Diethanolamine (DEA)	
Triethanolamine (TEA)	
Diglycolamine (DGA)	
Diisopropanolamine (DIPA)	
Methyldiethanolamine (MDEA)	

Scheme 1.2 represents the main reactions taking place during chemisorption of H_2S by a primary amine, such as MEA:

Ionization of Water: $H_2O = H^+ + OH^-$

Ionization of dissolved H_2S: $H_2S = H^+ + HS^-$

Protonation of Alkanolamine: $RNH_2 + H^+ = RNH_3^+$

Scheme 1.2: The basic ionic reactions involved in H_2O-Amine-H_2S system

The species mainly present in H_2S-rich alkanolamine solutions are the undissociated molecules H_2O, H_2S, and RNH_2 and the ions H^+, OH^-, HS^-, and RNH_3^+. The above reactions are applicable to secondary and tertiary amines as well. Supplementary reactions may occur such as dissociation of bisulfide (HS^-) to produce sulfide ions (S^{2-}). The equilibrium concentration of molecular H_2S in solution is

proportional to its partial pressures in the gas phase (i.e., Henry's law applies). So ionization of dissolved H_2S increases with increase in H_2S partial pressure. Also, vapor pressure of absorbed H_2S increases rapidly with the rise in temperature. It is therefore possible to strip absorbed gases from aqueous alkanolamine solutions by simple distillation.

Some sterically hindered amines such as N-tertiarybutyl diethylene glycolamine or TBGA can have advantages over MDEA with regard to selectivity but they are found to be too expensive for common industrial use (Cai et a, 1992). Structural formulas of some sterically hindered amines are shown in Table 1.3 (Sartori et al. 1983).

The properties of different alkanolamines and the advantages and disadvantages are listed in Table 1.4 and Table 1.5 respectively. From the tables it is clear that MDEA is superior to all alkanolamines in selective absorption of H_2S in present of many other gases. So, the present research is focused on H_2S chemisorption in MDEA only.

Table 1.3 Different sterically hindered amines used for H_2S removal (Sartoni et al. 1983)

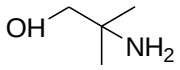
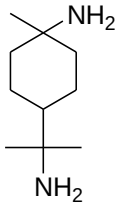
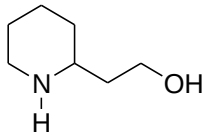
Amines	**structure**
2-amino-2-methylpropan-1-ol (AMP)	
1,8-Diamino-p-menthane (MDA)	
2-piperidine ethanol (PE)	

Table 1.4 Physical properties of alkanolamines (Kohl, 1997)

Property	MEA	DEA	TEA	MDEA	DIPA	DGA
Mol. Weight	61	105	149	119	133	105
Sp. Gr. 20 ^{o}C/20 ^{o}C	1.0179	1.0919	1.1258	1.0418	0.9890	1.0550
Boiling pt. (^{o}C) 760mmHg	171	decompose	360	247.2	248.7	221
Vapour Pressure, mmHg at 20 ^{o}C	0.36	0.01	0.01	0.01	0.01	0.01
Freezing pt (^{o}C)	10.5	28.0	21.2	-21.0	42.0	-9.5
Solubility in water (wt%) at 20 ^{o}C	Complete	96.4	Complete	Complete	87	Complete
Absolute viscosity, Centipoise, 20 ^{o}C	24.1	380	1013	101	198	26
Heat of Vapourization, kJ/kg at 1 atm (KJ/kg)	826	670	535	519	429	509

Table 1.5 Benefits and shortcomings in the use of different alkanolamines

Monoethanolamine (MEA)
Benefits • High solution capacity at moderate concentrations due to low molecular weight. • High alkalinity relative to other alkanolamines • Easy reclamation from the rich solution **Shortcomings** • Poor selective H_2S absorption of from acid gas streams containing other gases • Excessive chemical losses due to the formation of irreversible reaction products with gases containing COS and CS_2. • Aqueous MEA solution is more eroding than other alkanolamines for concentration exceeding 20% and high concentration of acid gases. • High energy consumption for stripping due to high heat of reaction with acid gases
Diglycolamine (DGA)
Benefits o Can be used in relatively high concentrations due to its low vapor pressure - causing lower circulation rates in comparison to MEA. o Can operate at high ambient temperatures –can purify large volumes of low pressure acid gas. o Relatively lesser capital and operating cost in comparison to MEA o Can result in partial removal of COS o Reclamation of DGA from the degradation products resulting from reactions of DGA with CO, and COS is possible by steam distillation. **Disadvantages** • MDEA is more selective than DGA
Diisopropanolamine (DIPA) **Benefits** • Substantial amounts of COS along with H_2S and CO_2 can be removed without damaging effects to the solution. • Steam requirements is low for regeneration of DIPA. **Shortcomings**

• MDEA is more selective than DIPA
Methyldiethanolamine (MDEA)
Benefits ➢ Absorption selectively for H_2S from acid gas streams is higher than other alkanolamines. ➢ Energy consumption during regeneration is compared to MEA and DEA. ➢ MDEA can be used in high concentration in aqueous solutions without appreciable amount of vapor loses. ➢ Less corrosive than MEA and DEA **Shortcomings** ➢ MDEA is more expensive than some other simple amines like MEA and DEA.

1.4 Utilization of H_2S

There are many ways to recover and utilize H_2S present in the gas stream, such as, Claus process, Crytasulf process etc. Few of them are discussed below:

1.4.1 Claus process

The Claus tail-gas clean-up process is the conventional process used for the elemental sulfur production from H_2S (Fig. 1.9). Carl Friedrich Claus first patented this process in 1983. This process recovers elemental sulfur from H_2S present in natural gas and in the tail gas stream that evolved after refining the crude oil.

Description of the Claus technology

Sour gasses having H_2S content around 25% are considered suitable for sulfur recovery through Claus process. The overall reaction can be written as:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O$$

A schematic diagram of a Claus process is presented in Fig. 1.9. The process is having mainly two steps, thermal and catalytic.

1. **Thermal step**

In this step, combustion of H_2S is done at above 850 ^oC. Then Claus gases having no other combustible content except H_2S, are burnt in central muffle surrounded by lenses. The combustion reaction can be written as:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$

This step is strongly exothermic and flame free that oxidizes hydrogen sulfide into sulfur dioxide. The next most important reaction of the process is:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The overall reaction can be written as:

$$10H_2S + 5O_2 \rightarrow 2H_2S + SO_2 + \frac{7}{2}S_2 + 8H_2O$$

The above equation shows that maximum conversion of H_2S into elemental sulfur is done in thermal step only.

2. **Catalytic Step**

In the catalytic step activated aluminium (III) and titanium (IV) oxides are used to enhance the product yield. The reaction in this step can be written as:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

This sulfur forms can be S_6, S_7, S_8 or S_9.

The primary procedure venture in the reactant stage is the gas heating procedure. It is important to avert sulfur condensation in the catalyst bed, which can be the cause of catalyst fouling. Claus process gives sulfur recovery of about 99%, which is remarkable indeed.

However, the Claus process is having number of unavoidable disadvantages for e.g.,

- If the concentration of CO_2 is high in the feed gas stream, it has to be pre-treated, which makes the process expensive.
- High temperatures operations.
- The process control for keeping the O_2/H_2S ratio should be exact.
- Maintenance cost of the Claus unit is very high.
- High sulfur content in the gas coming out from the Claus unit.

1.4.2 Crystasulf process

In this process, effective treatment of gasses containing high concentration of H_2S is performed. This process is used in the energy industry to handle sulfur amount between 0.1 and 20 tons per day.

The process removes H_2S from the sour gas stream and converts it into elemental sulfur using modified liquid-phase Claus reactions:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

H_2S is removed from the gas stream in a counter current absorber using heavy hydrocarbon liquid and then reacts with sulfur-di-oxide to yield elemental sulfur slurry which is then removed using filtration process.

1.4.3. Liquid phase oxidation processes

In mid-nineteenth century, gas purification using liquids in regenerative cycles has been initiated to produce pure elemental sulfur. Acid gases containing high CO_2/H_2S ratio can better be processed in liquid phase absorption/oxidation route than absorption/stripping route. Potential shortcomings of the process are the comparatively low absorption capacities of the solutions for H_2S and O_2 that can cause in huge liquid flow rates, the difficulty of extracting elemental sulfur from the liquid mix, and dissipation of heat generated during H_2S oxidation.

In early days, a slurry of iron oxide in a mildly alkaline aqueous solution was used for conversion of H_2S in liquid phase to sulfur. Later on, iron cyanide and thioarsenates based processes have been commercialized. Even though arsenic-based process was effective, it has lost market because of toxicity present in the scrubbing liquid. Also in 1970, quinone with vanadium salts was evolved as a highly successful liquid phase oxidant for H_2S. Environmental concerns about vanadium based processes have later made iron-chelate based processes like LO-CAT and Sulferox evolve in H_2S-removal market.

1.5 Knowledge gap and methodology of current work

There is no study on the use of H_2S absorbed in the widely used alkanolamine, MDEA to synthesize any fine chemicals like organic sulfides or disulfides. In many

petroleum and natural gas industries, where MDEA is primarily used as a sole absorbing agent, an alternative can be visualized to utilize the H_2S-laden MDEA as a sulfiding agent to synthesize organosulfur fine chemicals from organic halides. The present investigation is based on the methodology that H_2S-laden MDEA would be used to synthesize thioethers like DBS and organic disulfides like DBDS etc.

The two major reactants in the current study form different phases which are immiscible in nature. H_2S-laden MDEA forms an aqueous phase and benzyl chloride in toluene (solvent) forms organic phase. To bring them in contact with each other, phase transfer catalyst (PTC) can be employed. PTC helps in enhancement of the reaction as well as selectivity of desired products in the multiphase reaction. Quaternary salts have been found to be used widely for that purpose. In the current study, both nitrogen containing (amberlite IR-400) and phosphorous containing PTCs (tetrabutylphosphonium bromide (TBPB), trihexyl(tetradecyl)phosphonium chloride (THTDPC)) have been employed. Also, ambelite IR-400 is an insoluble solid catalyst and forms liquid-liquid-solid (L-L-S) system. Both conventional PTC, TBPB and ionic liquid (IL), THTDPC form liquid-liquid (L-L) systems. L-L PTC systems provide faster reactions, but catalyst recovery is difficult. L-L-S PTC systems are slower in comparison to L-L PTC, but it provides easy catalyst separation and reuse.

1.6 Industrial application of the products

The synthesis of thioethers using different reagents is a widely used method in the field of organic [19] and medicinal chemistry [20]. DBS has many important applications such as refining and recovery of precious metals, anti-wear additives for the high-pressure lubricants, stabilizers for photographic emulsions and few applications in the various anti-corrosive formulations [12]. Dibenzyl disulfide (DBDS) is very important chemical compound having very diversified applications in the field of organic synthesis. DBDS is used in manufacturing corrosion inhibitors, fragrance compounds, high-pressure lubricant additives and other organic compounds.

1.7 Origin and objective of the present work

The present work uncovered a range of interesting alternative to the Claus process to utilize H_2S existing in the different gas streams in the efficient manner. Due to few

drawbacks of Claus technology such as high energy consumption, complexity of the process and high rate of production of elemental sulfur as compare to that of consumption, development of an alternative process is a rising demand.

The present research effort uncovers the route for synthesis of value-added organosulfur fine chemicals by consuming H_2S present in various by-product gas streams. Dibenzyl sulfide and dibenzyl disulfide were synthesized from the aqueous H_2S-rich alkanolamines. The main aim of the current research can be summarised as follows:

- Synthesis of various organic sulfides like dibenzyl sulfide and dibenzyl disulfide from H_2S-rich alkanolamine like monoethanolamine and methyldiethanolamine under liquid-liquid (L-L) and liquid-liquid-solid (L-L-S) phase transfer catalysis (PTC) using tetrabutylphosphonium bromide (TBPB), trihexyl(tetradecyl)phosphonium chloride (THTDPC) and amberlite IR-400 as a phase transfer catalyst.
- Parametric study: effect of various process controlling parameters (stirring speed, catalyst concentration, reactant concentration, temperature, sulfide concentration, alkanolamine concentration, reaction time and temperature) on the conversion of reactant and selectivity of the desired product.
- Formulating a suitable reaction mechanism to explain the course of the reaction
- Investigation of the reusability of the solid catalyst in case of solid catalyst used.
- Development of the kinetic model and its validation against experimental data.

1.8 Phase transfer catalysis

Many valuable reactions cannot be brought about because of an inability of reagents to come together which are present in two different phases. Phase transfer catalysis is a synthetic organic synthesis method to resolve this problem. In this process, a small quantity of a phase transfer agent is introduced into the reaction mixture which transfers one reactant across the interphase and makes the reaction possible to give the desired product without being consumed.

1.8.1 Mechanism of PTC

Stark (1971) suggested an extraction mechanism of PTC which is illustrated in Fig 1.1. According to this mechanism, the quaternary ammonium cation Q^+ of the PTC forms an ion pair Q^+Y^- with the anion of the reactant present in the aqueous phase. The nucleophile Q^+Y^- travels to the organic phase by crossing liquid-liquid interphase due to its highly lipophilic nature where it reacts with the organic reactant RX and gives the desired product RY. The catalyst again reforms as QX and goes back to the aqueous phase and the cycle proceeds continuously. This is the normal way how a ionic PTC performed and often termed as "normal phase transfer catalysis". However, throughout the thesis we have used "PTC" to indicate normal phase transfer catalysis.

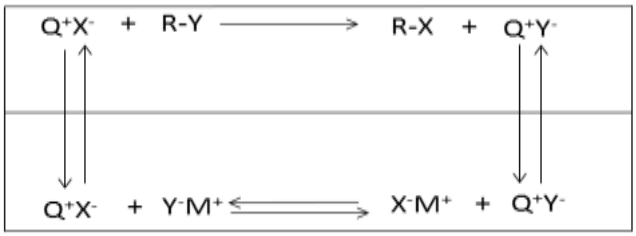


Figure 1.1. Extraction mechanism of phase-transfer catalysis

Besides the normal PTC reactions, the PTC technique could be applied to reactions involving electrophilic reactant cations, such aryldiazonium or carbonium and anionic catalyst, in which cationic reactant is continuously transferred from aqueous phase into organic phase in the form of a lipophilic ion pair, non-nucleophilic anionic catalyst, and reacts with second reactant from organic phase. This type of technique was called reversed phase transfer catalysis (RPTC). A complementary methodology named by Mathias and Vaidya (1986) as "inverse phase transfer catalysis (IPTC)" involves the conversion of reactant in organic phase to an ionic intermediate which is transported into the water.

1.8.2 Choice of PTC

The major factors while choosing a suitable PTC (Starks & Liotta, 1978) are:

- The PT catalyst must be cationic and should have good partition coefficient between the phases
- It should have loose cation-anion bonding to give high reactivity.

- The catalyst should be stable under the reaction conditions.
- The activity of the catalyst should be high enough.

1.8.3 Phase transfer catalyst

The most commercially used phase transfer catalysts are onium salts (ammonium and phosphonium salts), crown ethers, aza-macrobiocyclic ethers (cryptands) and polyethylene glycols (PEGs). Table 1.6 shows few properties of the commonly used PTCs.

Quaternary ammonium and phosphonium salts are extensively used and industrially most practicable PTCs. Crown ethers and cryptands are also widely used in solid-liquid reaction systems on the ground of their ability to form complex and solubilize metal cation and corresponding anion together to keep the charge balance maintained. But due to their high cost and toxic characteristics, they are not considered as very efficient for most of the industrial applications (Naik & Doraiswamy, 1998).

PEGs and their derivatives are also used as PTCs (Totten & Clinton, 1988). As compare to onium salts and crown ethers, PEGs are less active but they are relatively less expensive, stable and environmentally safe. It can be concluded that quaternary onium salts are most suitable option for organic synthesis as PTCs.

Table 1.6 Properties of commonly used PTC (Naik & Doraiswamy, 1998)

Catalyst	Cost	Stability and activity	Use and recovery of catalyst
Ammonium Salt	Cheap	Moderately active. Decomposes by reaction 1.1 at 100^0C and reaction 1.2 shown above.	Commonly used but difficult to recover.
Phosphonium salt	Costlier than ammonium salts	Moderately active. Thermally more stable than ammonium salt but decomposes under basic condition.	Commonly used but difficult to recover.

Crown ethers	Expensive	Highly active. Stable at both high temperature and basic condition.	Often used. Difficult to recover due to toxicity.
Cryptands	Expensive	Highly active. Stable at both high temperature and basic condition.	Used sometimes due to high activity. Recovery is difficult due to toxicity.
PEG	Very cheap	Lower activity but more stable than onium salts.	Rarely used where a high concentration of catalyst does not affect the synthesis reaction. Easy to recover.

1.8.4 Classification of PTC

PTC can be classified mainly in to two categories - insoluble and soluble PTC as shown in Fig 1.2. Further soluble PTC can be classified as liquid-liquid (L-L PTC), gas-liquid (G-L PTC) and solid-liquid PTC (S-L PTC). Product separation is difficult and catalyst cannot be reused in case soluble PTC and this drawback can be overcome in insoluble PTC.

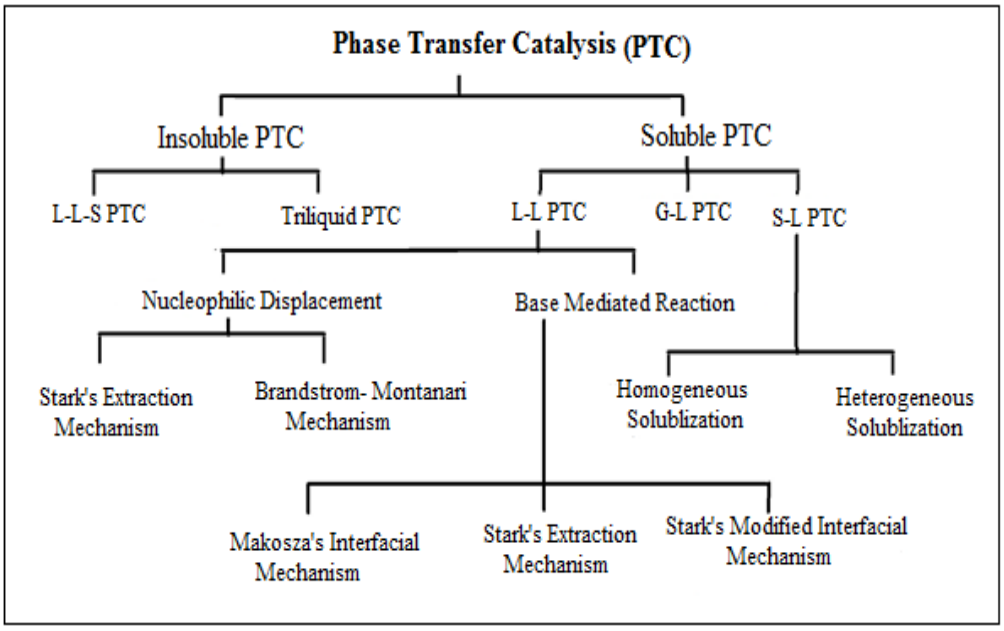


Figure 1.2: Classification of PTC

1.8.5 Soluble PTC

1.8.5.1 Liquid-liquid (L-L) PTC

There are two mechanistic model to explain L-L PTC namely Stark's extraction mechanism and Branstrom-Montanari modified starks extraction mechanism. According to Stark's extraction mechanism (Fig 1.3) the PTC has both organophilic and hydrophilic characteristics and can distribute itself between both organic and aqueous phase. The anions of reactant and product can cross the interphase and transfer into the organic phase as a complete cation-anion pair.

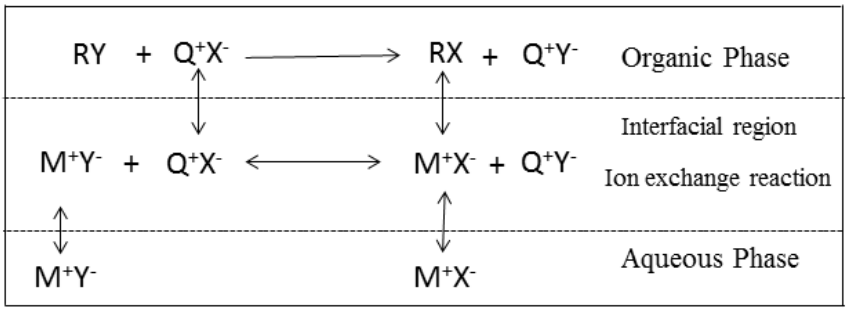


Figure 1.3. L-L PTC: Brandstrom-Montanari modification of Stark's extraction mechanism

Brandstrom-Montanari mechanism (Starks, Liotta, & Halper, 2012) is the modified Stark's extraction mechanism which says that the PTC is a highly organophilic one and stays in the organic phase only (Scheme 1.4). In that case, the ion-exchange reaction takes place at the interphase and synthesis reaction takes place in the organic phase.

1.8.5.2 Solid-liquid (S-L) PTC

The mechanism of S-L PTC was proposed by Melvilla and Goddard in 1988 (Melville & Goddard, 1988). According to this mechanism given in Fig 1.4 (a), the cation Q^+ of catalyst directly reacts with the solid surface of the inorganic salt to form the soluble anionic species. But as demonstrated in Fig 1.4 (b), the anionic species first dissolves in the solution and then makes an ion-pair with the catalyst cation. If the inorganic salt is very slightly soluble, then Fig 1.4(a) will be dominant but if the salt possesses substantial solubility then Fig 1.4(b) is to be expected.

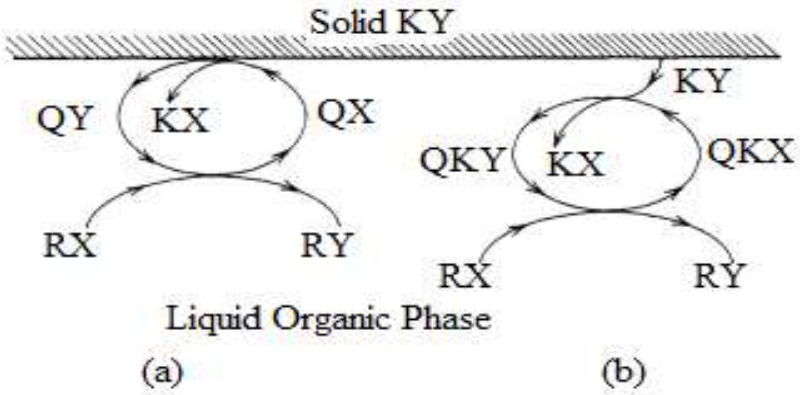


Figure 1.4. Mechanism of Solid-Liquid PTC

1.8.5.3 Gas-liquid (G-L) PTC

In G-L PTC reactions, the gaseous phase contains an organic substrate and passes over the solid inorganic reactant coated with PTC in a semi-liquid form as shown in Fig. 1.5.

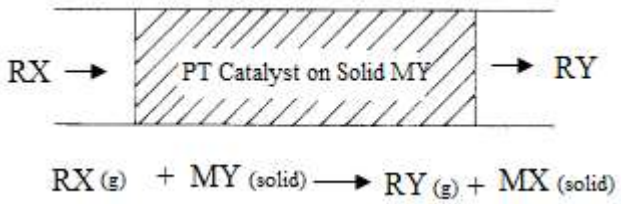


Figure 1.5. Mechanism of G-L PTC

The few advantages of G-L PTC over L-L PTC are a) its continuous mode of operation through a constant flow of organic gaseous reactant over a solid bed, b) PTC can be easily recovered as it is directly loaded on an inorganic solid bed and c) increased selectivity is obtained due to the absence of unwanted side reaction.

In a G-L process, very high energy requirements are needed to carry out the process in gaseous form which may be responsible for the thermal decomposition of the catalyst. Therefore, the catalyst must be thermally stable (Tundo et al. 1989).

1.8.6 Insoluble PTC

In soluble PTC systems, separation of catalyst and product from the reaction mixture is done by some unit operation like distillation, extraction and absorption which

makes the process energy expensive. Therefore, the catalyst is generally considered to be a waste as it is smaller in quantity than the product. These problems can be overcome by introducing insoluble phase transfer catalysts. The system can be divided into two categories named as Liquid-Liquid-Solid (L-L-S) PTC and Liquid-Liquid-Liquid (L-L-L) PTC.

1.8.6.1 Liquid-Liquid-Solid (L-L-S) PTC

Liquid–Liquid–Solid (L-L-S) triphase catalysis has huge operational advantages as its separation is easy so that it can be regenerated and reused efficiently. In L-L-S PTC, one of the reactant gets adsorbs into the catalyst and makes an active site and the other reactant directly reacts with it. Ion-exchange step takes place in aqueous phase and substitution step takes place in the organic phase as shown in Fig. 1.6 (Wu & Wang, 2003). In L-L-S PTC, the catalyst is supported on a polymer or inorganic support and can be separated by filtration from the reaction mixture and reused but there is a loss in activity due to binding of catalyst on the solid surface which results in lower reaction rates due to intraparticle diffusion limitations (Yadav & Reddy, 1999).

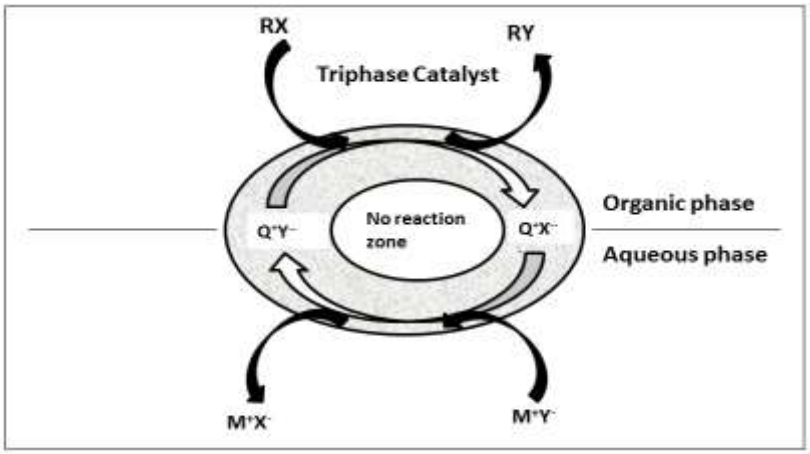


Figure 1.6. Mechanism of L-L-S PTC

1.8.6.2 Liquid-Liquid-Liquid (L-L-L) PTC

In L-L PTC, the recovery and reusability of the catalyst is difficult which is a major environmental concern (Yadav & Lande, 2005). The problem can be overcome by using L-L-L PTC.

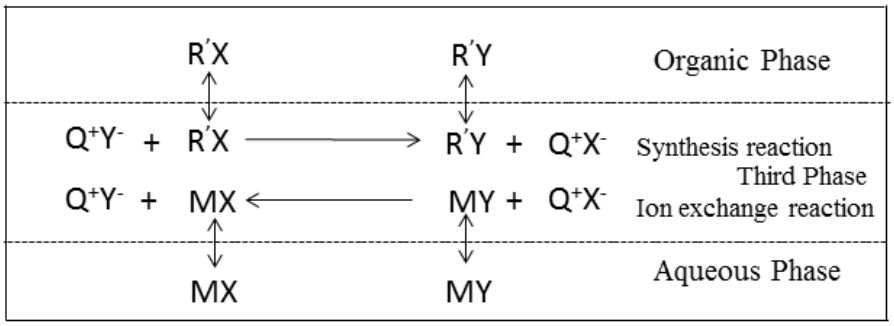


Figure 1.7. Liquid-Liquid-Liquid PTC mechanism

In L-L-L PTC, the third phase is rich in catalyst and has limited solubility in both organic and aqueous phases. In this system reaction occurs in the catalyst rich third phase and the catalyst can be reused without loss in catalytic activity. The selectivity in case of L-L-L PTC is better. Instead of these advantages, few disadvantages are also there with L-L-L PTC. A very high amount of catalyst is generally required, which is expensive and the method is not applicable for systems where a very high temperature is required to carry out the reaction. As the temperature increases, the stability of third liquid phase decreases.

1.9 Organization of the thesis

The complete thesis is presented in seven chapters. All chapter starts with abstract and well-defined introduction and ends with conclusion.

Chapter 1 incorporates different sources of H_2S, its adverse effects, removal techniques and the scope of the present work.

Chapter 2 deals with the literature review on the work done related to the present work till date and the research gap.

Chapter 3 describes the experimental procedure opted to reach the goal, the chemicals used and the description of analytical work done using GC-MS and GC-FID.

Chapter 4 defines the first system on the synthesize DBS from the reaction of benzyl chloride (BC) and H_2S-Rich Aqueous Methyldiethanolamine (MDEA) under liquid-liquid phase transfer catalysis (L-L PTC).

Chapter 5 is based on the detailed kinetic investigation and the selective synthesis of dibenzyl sulfide (DBS) from the reaction of aqueous H_2S-rich Methyldiethanolamine

(MDEA) with benzyl chloride (BC) under liquid-liquid phase transfer catalysis (L-L PTC).

Chapter 6 deals with the detailed kinetic investigation for the selective synthesis of dibenzyl disulfide (DBDS) from the reaction of benzyl chloride (BC) and H_2S-rich aqueous monoethanolamine (MEA) under liquid-liquid-solid phase transfer catalysis (L-L-S PTC).

Chapter 7 presents the overall conclusion and recommendations for further research.

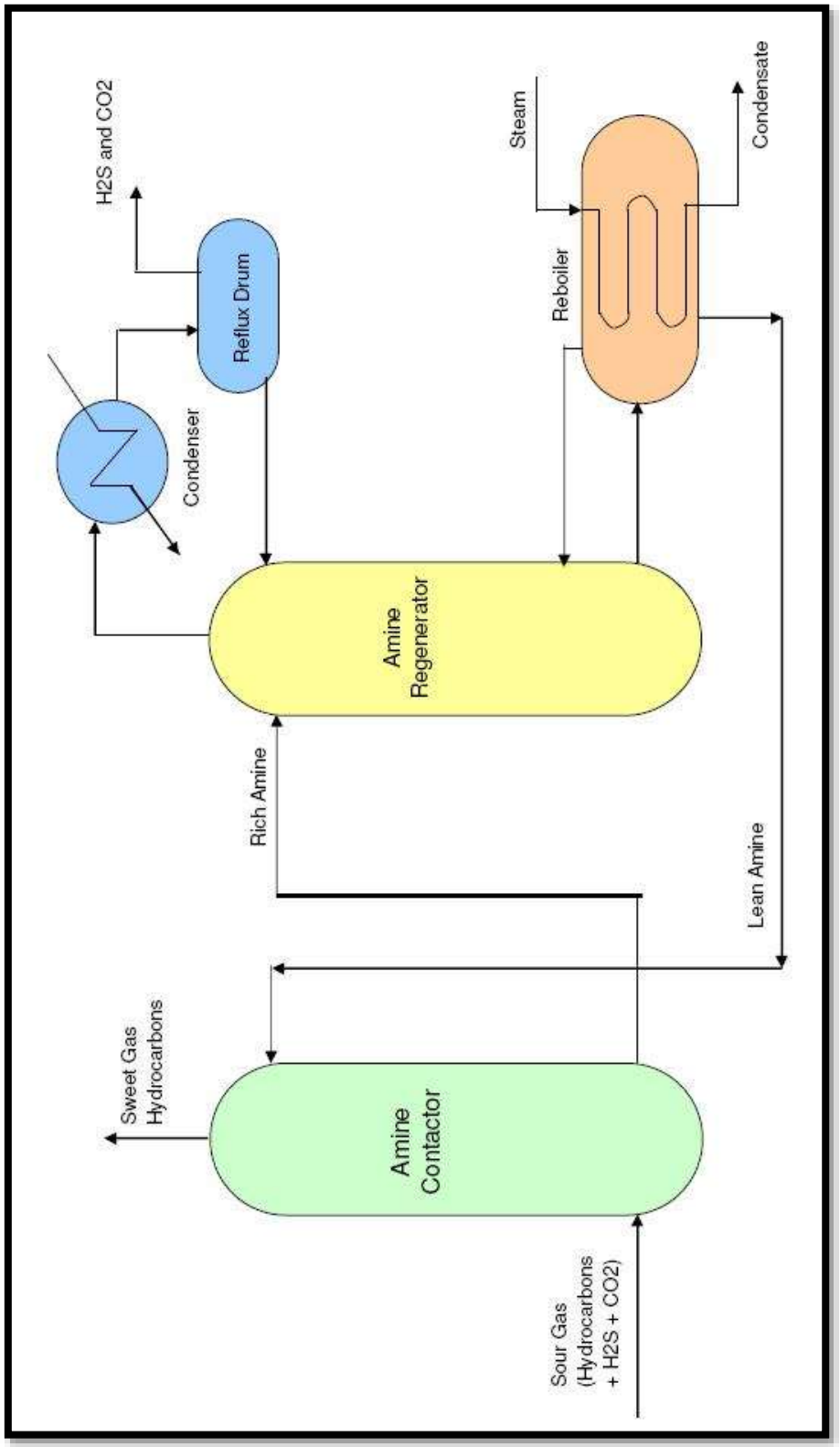


Figure 1.8: Amine Treating Unit

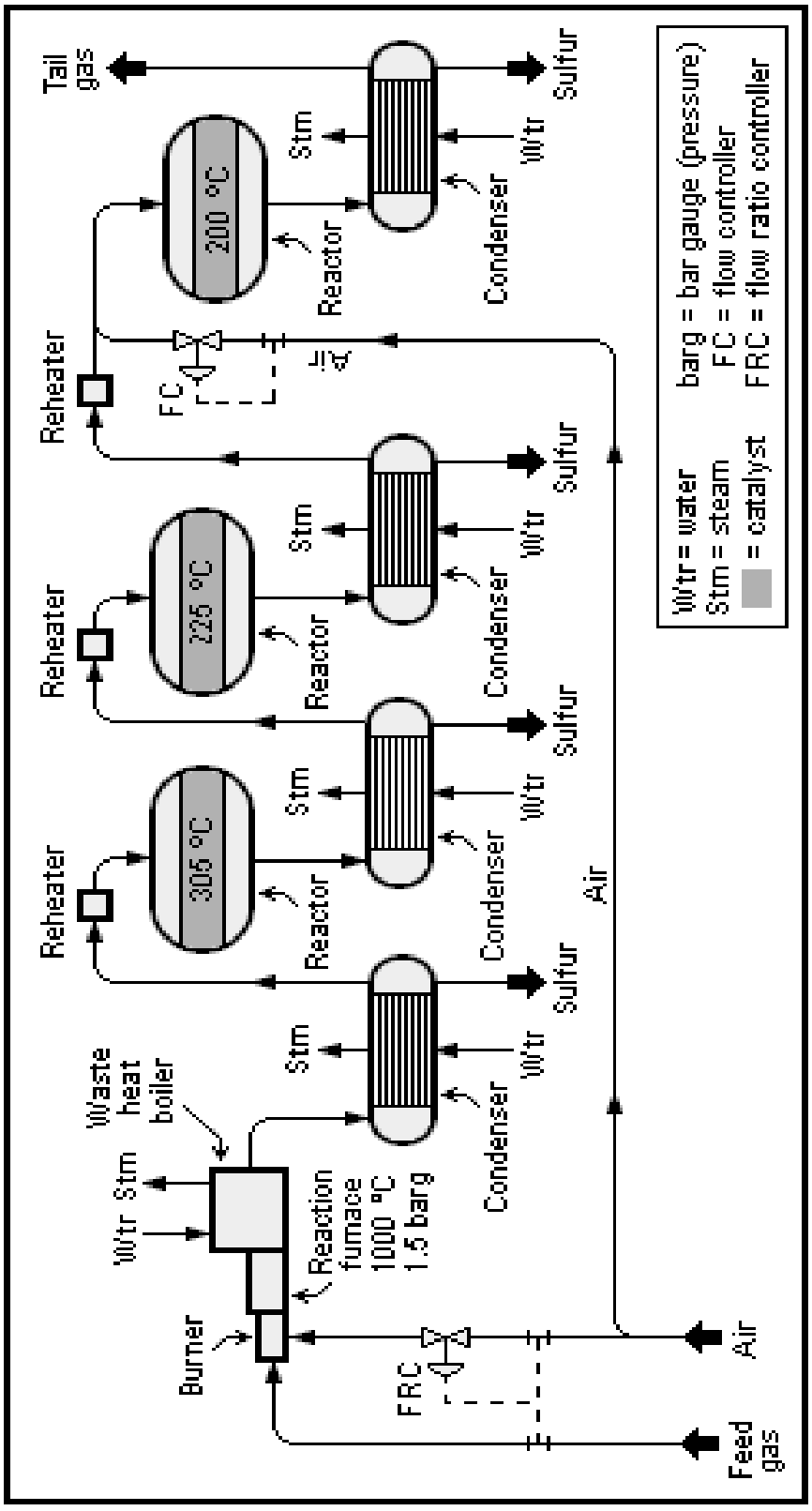


Figure 1.9: Sulfur Recovery Using Claus Unit

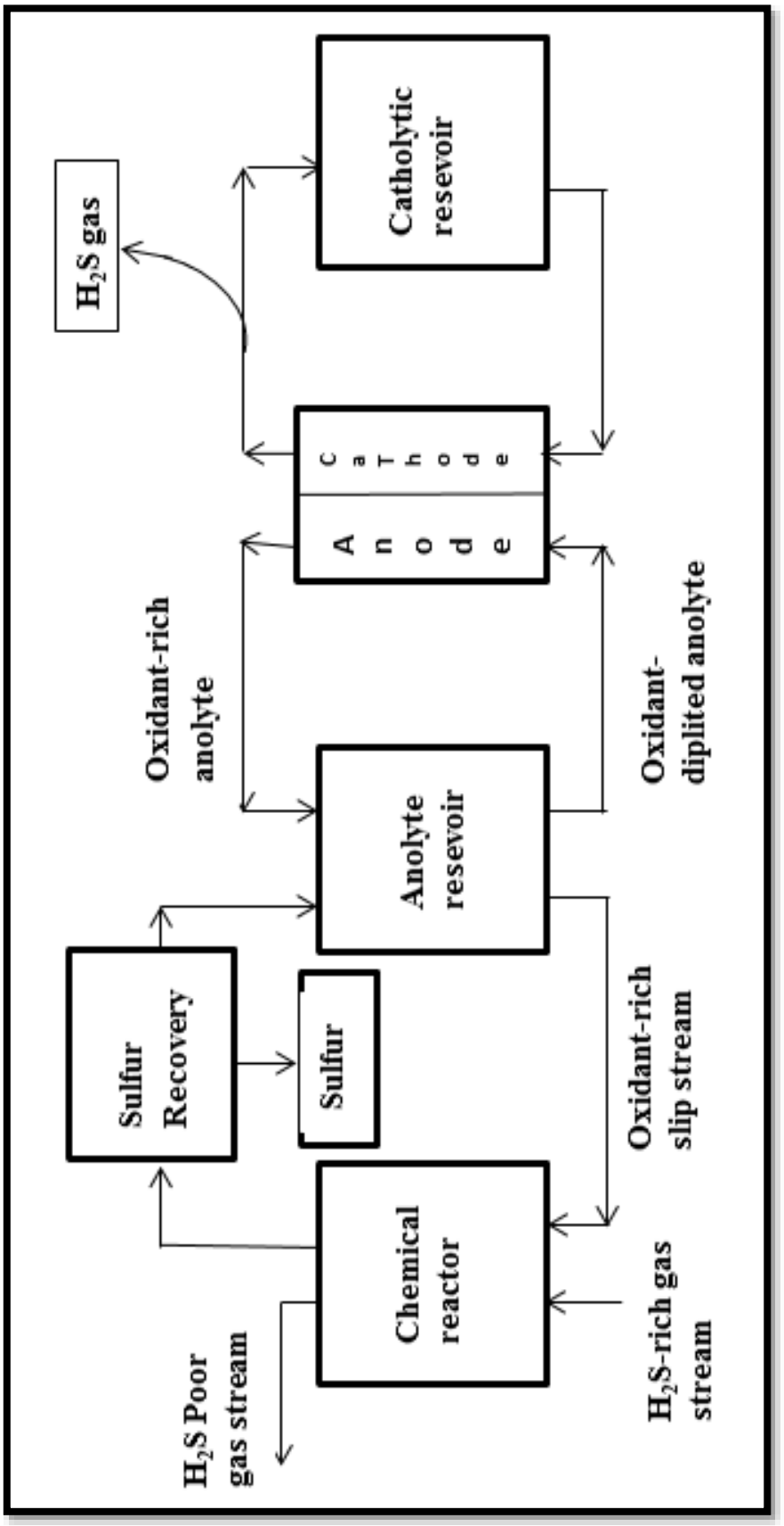


Figure 1.10: H_2S Utilization Using Acidic Electrochemical

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Chapter 2

Literature Review

This chapter deals with the literature review related to the removal, recovery and utilization of hydrogen sulfide obtained from various gas streams, synthesis of different organic sulfides including dibenzyl sulfide and dibenzyl disulfide and application of different types of phase transfer catalysts.

2.1 Removal of hydrogen sulfide

The necessity of removal of H_2S from various gas streams is already discussed in Chapter 1. Various methods are there which are having industrial applications for the removal of H_2S, such as, adsorption, absorption and membrane-based processes. There is a plenty of literature available on removal of H_2S from various gas streams using various methods as given below:

2.1.1 Adsorption processes

Elyassi et al. (2014) used mesoporous silica supported by copper-zinc oxide as an adsorbent for H_2S removal. Malamine and urea impregnated modified bituminous activated coal-based carbon heat treated at 650-850^{0}C is found to be an efficient adsorbent for H_2S removal. Some other adsorbents like alum water (Wang & Pei, 2012), activated carbon (Ghosh & Tollefson, 1986; Kaliva & Smith, 1983), silica-alumina (Tagliabue et al., 2012), nitrogen modified carbide-derived carbons (Seredych, Portet, Gogotsi, & Bandosz, 2009) and silica polymer based carbon composites (Bandosz, Seredych, Allen, Wood, & Rosenberg, 2007) were also used for H_2S removal. Carbonated-rich bentonite modified by iron and copper chloride (Stepova, Maquarrie, & Krip, 2009) Microporous (Touefson, 1986) carbons (Mee, Trimm, & Cant, 1997) showed a high degree of H_2S removal efficiency. Ansari et. al. (2010) used a mixed dewatered sewage sludge derived adsorbent with polystyrene sulfonic acid-co maleic acid sodium salt in the ratio of 10:90, 30:70, 50:50 and 70:30 and carbonized the sample at 950^{0}C, then washed it with water to remove the excess amount of salt and proved that addition of polymer with sludge enhances the H_2S adsorption.

2.1.2 Biological processes

Microbiological treatment of H_2S is done by many researchers, but only very few of those processes have been proven on a large scale (Jensen & Webb, 1995). *Chlorobium Limcola* (Ball, Nedwell, & Perkins, 2007), *Thiobacillus Thioparus* CHII, *Acinetobacter sp. MU_03* and *Alcoligenes Faecalis* MU2_03 (Potivichayanon, Pokethitiyook, & Kruatrachue, 2006), photosynthetic bacteria (Kobayashi, Stestrom, & Mah, 1983), *Thiobacillusthioparus* (Oyarzu, Arancibia, & Canales, 2003) and *Thiobacillusdenitrificans* (Sublette & Sylvester, 1987) are the microorganisms used for biological treatment of H_2S.

2.1.3 Membrane-based processes

Although the traditional packed bed absorbers have been used in the chemical industry for decades, there are several disadvantages such as flooding at high flow rates, unloading at low flow rates, channeling, and foaming, which lead to difficulties in mass transfer between gas and liquid.

The use of membrane technology for the removal of H_2S from the gas streams is well documented. This process is having several advantages, such as, larger interfacial area per unit volume, self-governing control of gas and liquid flow rates without flooding, loading, foaming, etc. (Ahmed & Semmens, 1992; Cooney & Jackson, 1989; Costello, Fane, Hogan, & Schofield, 1993; Kreulen, Smolders, Versteeg, & van Swaaij, 1993; Qi & Cussler, 1985; Yang & Cussler, 1986). Hollow fiber membrane has huge application in the field of H_2S removal (Chenar, Savoji, & Soltanieh, 2011; Lv, Yu, Tu, Yan, & Dahlquist, 2012; Marzouk, Al-marzouqi, Teramoto, Abdullatif, & Ismail, 2012; Wang, Teo, & Li, 2002). Li et al. (1998) successfully removed H_2S from the gas stream using an asymmetric hollow fiber membrane modules and concentrated alkaline solution together, and the preparation of hollow fibres was done from polysulfone/N-methyl-2-pyrrolidone/1-propanol and polyethersulfone/N-methyl-2-pyrrolidone/ethanol polymer solutions. The range of concentration of H_2S in the feed varied between 16-24 ppm that contacted countercurrently on the shell side with 10% NaOH solution. A dried cellulose ester membrane also used for treating a gas having permeability for H_2S and CO_2 and the method was invented by (Cooley, 1977). Catalytic platinum-based membrane reactor

(Edlund & Pledger, 1994), amorphous silica membrane reactor (Akamatsu, Nakane, Sugawara, Hattori, & Nakao, 2008), porous vycor glass membrane reactor (Kameyama, Dokiya, Fujishige, Yokokawa, & Fukuda, 1981) showed significant results for H_2S removal.

2.1.4 Absorption processes

The absorption process is a technology that can be easily installed with existing power plants, and industry can be retrofitted with equipment for absorption; whereas other process technologies for H_2S removal involves new forms of power plant technology.

Efficient removal of H_2S from gas stream was also done using an aqueous metal sulfate absorbent (Ter Maat, Hogendoorn, & Versteeg, 2005) and calcium carbonate–based solid waste containing some other elements such as Mg, Al, Fe, Si, Cl, Na etc. (Xuan, Minh, Martinez, Nzihou, & Sharrock, 2015) as an absorbent. Hamblin (1973) (Haniblin, Deerfield, 1973) developed a process for H_2S removal using ammonium hydroxide that includes scrubbing of gas streams with ammonium hydroxide, catalytic treatment of effluent stream with air stream produces ammonium polysulfides and further treatment of polysulfides produces elemental sulfur. A cost effective and environmentally acceptable method was developed (S. R. Knight, 1981). Removal of H_2S from gas streams and its conversion into sulfur by treating it with a nitrohumic acid and its salts derived from the treatment of humic acid with a nitrating agent is also an interesting invention (Toyama & Ishizaki, 1976).

Alkanolamines are nowadays having wide industrial applications (K. M. Brown, 1965; Sartori, Linden, & Leder, 1980). Alkanolamine based separation process is commercially well-adopted as it has several advantages over the ammonia-based process, as alkanolamines have less vapour pressure that favoursflexible process operation (in terms of pressure, temperature, concentration of alkanolamine), recycling is easy, and loss of solution due to vaporization is minimum (Kohl & Nielsen, 1997; Mandal & Bandyopadhyay, 2006). The credit for development of alkanolamines based process for gas purification goes to R. R. Bottoms (1930) who was the first, granted a patent on purification of gases using triethanolamine (TEA) (Kohl & Nielsen, 1997) but due to less absorption capacity, TEA was found to be relatively less attractive. Primary, secondary and

tertiary are the three important categories of alkanolamines. The most commonly used primary, secondary and tertiary alkanolamines are monoethanolamine (MEA) (Al-Baghli, Pruess, Yesavage, & Selim, 2001; Kaewsichan, Al-Bofersen, Yesavage, & Selim, 2001), diethanolamine (DEA) (Maity, Pradhan, & Patwardhan, 2006a) and methyldiethanolamine (MDEA) (B. Mandal & Bandyopadhyay, 2006) respectively. Among these alkanolamines, MDEA is widely used as sour gas treating agent because it possesses some advantages, such as, higher absorption capacity, lower regeneration energy, minimum corrosion effect, reduced solvent loss due to less vapour pressure, chemically stable and economically beneficial (Al-Baghli et al., 2001; Kaewsichan et al., 2001; Kohl & Nielsen, 1997; Maity et al., 2006a; B. Mandal & Bandyopadhyay, 2006; Sen, Pradhan, & Patwardhan, 2011; Singh et al., 2016; R H Weiland, Sivasubramanian, & Dingman, 2003). Also, MDEA is more selective than MEA in the absorption of H_2S in the presence of other gases like CO_2 (Mandal, Biswas, & Bandyopadhyay, 2004). There is quite a number of literature available on the study of equilibrium solubility of acid gases (H_2S + CO_2) and mathematical expressions representing solubility of acid gases in various alkanolamines were governed from experimental data (Al-Baghli et al., 2001; Austgen, Rochelle, & Chen, 1991; Bolhàr-Nordenkampf, Friedl, Koss, & Tork, 2004; Isaacs, Otto, & Alan, 1980; Kaewsichan et al., 2001; Lawson & Garst, 1976; Lee, Otto, & Mather, 1976; Rebolledo-Libreros & Trejo, 2004; Sadegh, Stenby, & Thomsen, 2015; Sidi-Boumedine et al., 2004; Vallée, Mougin, Jullian, & Furst, 1999; Weiland, Chakravarty, & Mather, 1993).

2.2 H_2S utilization

Various approaches have been developed for the utilization of H_2S. The conventional and well-established technology for the H_2S utilization is Claus technology which has been already discussed in Chapter 1. Various inventions have been done by modifying the Claus technology to make the process better (Etal, 1963; K.-T. Li, Min-Ya Huang, & Cheng, 1997a, 1997b). Despite conventional and well-practiced method, Claus technology has some flaws as well which we have discussed in Chapter 1. Due to these flaws an alternate process to the Claus technology is in high demand.

The conversion of hydrogen sulfide into elemental sulfur and hydrogen was done using acidic electrochemical process (D. W. Kalina & Maas, 1985). In this method iodide

oxidizes electrochemically in aqueous hydroiodide acid and hydrogen gas is produced concurrently with soluble triiodide while impure sulfur is produced by the reaction of H_2S with an electrolyte solution. The same work continued by the same authors using basic electrochemical process (Kalina & Maas, 1985) in which iodine is produced electrochemically and disproportionate to yield iodate that further reacts with H_2S to yield sulfur. Petrov et. al. (1996) produced extremely pure sulfur and hydrogen using chemical-electrochemical plants. H_2S has also been used as a fuel to examine the electrochemical characteristics and product distribution of a ceria-based solid-oxide fuel cell (Peterson & Winnick, 1998).

Very less amount of literature is available on the development of an alternative process to the Claus technology for efficient utilization of H_2S to synthesize value-added fine chemicals. In recent years few papers are published on the synthesis of fine chemicals like thioethers and organic sulfides and for the reduction of nitro compounds by utilizing H_2S (Maity et al., 2006a; Maity, Pradhan, & Patwardhan, 2006c, 2007, 2008; Sen, Maity, Pradhan, & Patwardhan, 2007; Sen et al., 2011; Singh et al., 2016).

2.2.1 Synthesis of thioethers

The synthesis of thioethers using different reagents is a widely used method in the field of organic (Baird & Rayner, 1998; Brown et al., 1999; Emond et al., 2002; Field, 1972; Procter, 2000; Saxena, Kumar, & Mozumdar, 2007; Winn et al., 2001) and medical chemistry (Hundscheld, Tandon, Rouwette, & Leusen, 1987; Ouertani, Collin, & Kagan, 1985; Pollard & Vederas, 2006). However, limitations of these methods are low yield, long reaction time and high operating temperatures. In the continuation an economic and eco-friendly one-pot synthesis method was developed for the synthesis of thioethers by the coupling of different alkyl/aryl halide with thiols using phosphotungstic acid (A. Kumar, Singh, Kumar, Chandra, & Mozumdar, 2007) and palladium on magnesium oxide (Corma, Navas, Rodenas, & Sabater, 2013) as a catalyst. An another efficient, simple and green method was developed for the synthesis of sulfides from alkyl/aryl thiols and different halides under catalyst and solvent-free conditions (Movassagh & Mohammad, 2009). Bandgar et. al. (2002) successfully developed a zinc-mediated method to prepare thioethers from alkyl halides and thiols (Bandgar, Pandit, & Nagargoje, 2002). An

improved and very mild method was also developed for the preparation of thioethers by S-alkylation of various alkyl/aryl thiols in the presence of DMF, tetrabutylammonium iodide (TBAI) and cesium carbonate (Salvatore, Smith, Nischwitz, & Gavin, 2005) and via trialkylborates (Gunes, Sirkecioglu, & Bicak, 2010). One another simple route was opted for the preparation of thioethers by 1, 2-adition of thiols to alkyl halides using silica nanoparticles as a reusable catalyst (Banerjee, Das, Alvarez, & Santra, 2010). A metal-free method was developed to prepare the thioethers by the coupling of thiols with tosyl hydrazones (Ding, Cao, Yuan, Liu, & Peng, 2011). Iridium complex was used for the first time to achieve the C-S cross coupling reaction of diaryl disulfides with aryl fluorides to synthesize thioethers (Li, Miao, & Ding, 2015). A new reductive indium-catalyzed synthesis of sulfides from thiols and esters was reported (Miyazaki, Nishino, Yoshimoto, Ogiwara, & Sakai, 2015). Recently, a process for the solvent free synthesis of thioethers was reported from the reaction of Michael acceptors with $\beta-$ acyloxy mercaptans (Abbasi & Khalili, 2016).

Among all of these thioethers, some research has been done on the selective synthesis of dibenzyl disulfide (DBS). DBS has many important applications such as refining and recovery of precious metals, anti-wear additives for the high-pressure lubricants, stabilizers for photographic emulsions and few applications in the various anti-corrosive formulations (Pradhan & Sharma, 1990). Some valuable synthetic intermediates such as dibenzyl sulfoxides and dibenzyl sulfone can also be prepared by oxidizing DBS (Mohammadpoor-baltork, Memarian, & Bahrami, 2005; Varma, 1997).

Pradhan & Sharma, (1990) prepared DBS from the reaction of benzyl chloride and sodium sulfide under solid-liquid (S-L) and liquid-liquid (L-L) phase transfer catalysis (PTC) using six different phase transfer (PT) catalysts. The same work continued by the same authors using basic aluminum oxide and amberlyst A27 (Cl^- form) as a PTC (Pradhan & Sharma, 1992). Tetrahexylammonium bromide was also used for the preparation of DBS (Ido, Susaki, Jin, & Goto, 2000). Zirconium tetrachloride ($ZrCl_4$) dispersed on dry silica gel was found a good reagent for the synthesis of DBS from the corresponding thiol under solvent free condition (Firouzabadi, Iranpoor, & Jafarpour, 2006). Lu & Cai, (2012) developed an odorless and efficient method to synthesize DBS from thiourea and benzyl chloride using Triton X10 aqueous micelles.

There are some reports available on the synthesis of DBS by the deoxygenation of sulfoxides using various reducing agents such as 2,6-Dihydroxypyridine (Miller, Collier, & Wu, 2000), N-bromosuccinimide (NBS), 2,4,4,6-tetrabromo-2,5-cyclohexadienone (Iranpoor, Firouzabadi, & Shaterian, 2002), Zirconium tetrachloride/sodium iodide ($ZrCl_4$/NaI) and $ZrOCl_2.8H_2O$/NaI (Firouzabadi, Iranpoor, & Jafarpour, 2005), Al-$NiCl_2 \cdot 6H_2O$ (Raju, Devi, Nongpluh, & Saikia, 2005), InI_3 and 1,1,3,3-tetramethyldisiloxane (Miyazaki et al., 2015) and InI_3 and hydrosilane (Miyazaki, Katayama, Yoshimoto, Ogiwara, & Sakai, 2016). However, there are some disadvantages with the reduction process to synthesize DBS, such as complex procedure, unforgiving acidic conditions, very high operating temperature, expensive reagents and long reaction times (Nasser Iranpoor et al., 2002).

A fascinating research on the synthesis of DBS by utilizing H_2S under PTC conditions is found in the literature. Sen et al. (2007) synthesized DBS from the reaction of BC and H_2S-rich monoethanolamine using tetrabutylammonium bromide (TBAB) as a PTC under L-L PTC condition.

2.2.2 Synthesis of organic disulfide

Dibenzyl disulfide is very important chemical compound and having a very diversified applications in the field of organic synthesis. Several methods have been described for the preparation of organic disulfides using different reagents and catalysts. Dhar synthesized disulfide by alkylation of alkyl halides with tetrathiotungstate and tetrathiomolybdates (Dhar & Chandrasekaran, 1989). Benzyltriethylammonium tetracosathio-heptamolybdate $[(C_6H_5CH_2N(Et)_3)_6Mo_7S_{24}]$ was found to be agood reagent for the synthesis of disulfide from alkyl halides (Polshettiwar, Nivsarkar, Acharya, & Kaushik, 2003). Disulfides were synthesized by oxidative coupling of thiols in the presence of air using Fe (III)/NaI as a catalyst (Iranpoor & Zeynizadeh, 1998). Thiols were oxidized into their corresponding disulfides through oxidative coupling in presence of potassium phosphate as a catalyst (Joshi, Bhusare, & Baidossi, 2005). Leino et. al. (2004) developed a method for the preparation of symmetrical disulfides by the addition of sulfuryl chloride with alkyl/aryl thiols in the ratio of 1:2 under a solvent free condition or in the solution of dichloromethane. Harpp et. al. (1986) prepared cyclic disulfides by bromination and iodination of alkyl thiolates. DBDS was also prepared by copper-

catalysed disproportionation of α-toluene in the three hours of reaction time giving yield of 99% (Choi & Yoon, 1996).

Dialkyl disulfides were formed by the reaction of alkyl halides with sulphur in alkaline medium in the presence of PEG400 (Wang, Wang, & Cui, 1995), PEG200 (Abbasi, Mohammadizadeh, & Taghavi, 2013; Firouzabadi, Iranpoor, & Abbasi, 2010) as a PTC and using sulfurated borohydride exchange resin under anhydrous conditions (Bandgar, Uppalla, & Sadavarte, 2001). Phase transfer catalyzed synthesis of disulfides was achieved by the reaction of corresponding alkyl halides with a mixture of sodium sulfide and sulfur in water-$CHCl_3$ (Hase & Perakyla, 1982). Sonavane also developed a one-pot method for the synthesis of disulfides from the reaction of sulfur withsodium sulfide in the presence of didecyldimethylamonium bromide (DDAB) as a PTC (Sonavane, Chidambaram, Almog, & Sasson, 2007; Sonavane, Chidambaram, Khalil, Almog & Sasson, 2008).

2.3 Multiphase reactions

In the field of organic synthesis, multiphase reactions are the very common phenomenon. If the reactants are present in two or more different phases, then the reaction process is called multiphase reaction. The phase contains one reactant can be in any state, such as liquid, solid or gas. In the absence of any catalyst, reactions occur at the interphase and proceeds very slowly. To obtain fast reaction and high product yield, it is necessary to introduce a substance to transport reactant from one phase to another phase by crossing an interphase. The substances having the ability to transport reactant from one phase to another are called phase transfer catalysts (PTC). An ample literature is available on the use of PTC in multiphase reactions (Lin & Yang, 2005; Satrio, Glatzer, & Doraiswamy, 2000; Tundo, Trotta, Moraglio, & Ligorati, 1988; Yadav & Lande, 2006b; Yadav & Purandare, 2005; Yang & Chen, 2009; Yang & Huang, 2011; Yang, Hung, & Tu, 2014; Yang & Li, 2006; Zhao, Sun, Liu, & He, 2015).

2.3.1 Phase transfer catalysis

Phase transfer catalysis is a technique to lead a reaction from the reactants present in two mutually insoluble phases under mild operating conditions. It is now a commercially mature discipline having a wide range of industries such as perfume, agrochemical, pharmaceutical and polymer industries (Sasson & Neumann, 1997; Starks, Liotta, & Halpern, 1994). Many organic compounds have been synthesized in the presence of different PTC (Sowbna & Yadav, 2012; Yadav & Lande, 2006b; Yadav & Motirale, 2010; Yadav & Sowbna, 2012).

We have had a detailed discussion on L-L PTC in Chapter 1. The research on organic synthesis using L-L PTC system has been carried out since a long time but it is also proving its enormous applications in modern trends.

Tetrabutylammonium bromide (TBAB) was employed for the efficient reduction of *p*-Chloronitrobenezene, *p*-nitroanisole, citronellal and nitrotoluenes under L-L PTC condition (Maity et al., 2006c; Yadav, Jadhav, & Sengupta, 2003a, 2003b; Yadav & Lande, 2006a). A successful synthesis of dichlorocyclopropane was done by the reaction of chloroform with styrene using triethyl benzyl ammonium chloride as a PT catalyst under L-L PTC condition (Sirovski, Gorokhova, & Ruban, 2003). Microwave irradiated o-alkylation of phenols was also achieved under L-L PTC condition using TBAB as a PTC (Yadav & Bisht, 2004, 2005). Benzaldehyde was synthesized from benzyl chloride using tetrabutylammonium chloride (TBAC), tetrabutylammonium hydroxide (TBAOH) and tetrabutylammonium acetate (TBAA) as a PTC under L-L PTC condition (Satrio & Doraiswamy, 2002). A very important thioether, DBS was also synthesized from the benzyl chloride with sodium sulfide using TBAB as a PTC (Maity, Pradhan, & Patwardhan, 2006b). The only disadvantage with L-L PTC is that the catalyst recovery and reusability is complicated (Yadav & Reddy, 1999).

A few scientific report explored tetrabutylphosphonium bromide (TBPB) as phase transfer catalyst in organic synthesis. 1-Nitronaphthalene has been selectively reduced by aqueous sulfide under liquid-liquid mode in present of TBPB (Mondal, Sen, & Singh, 2015). TBPB has also been found to be best among several other soluble N-containing and P-containing PTC in the synthesis of alkyl and arylthioglycosides and thiodisaccharides in a two-phase system (Fujihira, Takido, & Seno, 1999).

Involvement of ionic liquids (ILs) is well-appreciated as a replacement of traditional volatile solvents which are the major cause of environmental pollution (Welton, 1999) and for the traditional PTCs. ILs are having many other applications, such as, electrolytes for the batteries and fuels (Wilkes, Levisky, Wilson, & Hussey, 1982), in heavy metal ion extraction (Dai, Ju, & Barnes, 1999; Visser et al., 2001; Visser, Swatloski, & Rogers, 2000) and most importantly as a PTC for the synthesis of value-added fine chemicals. The advantages of ILs are – very less volatility, negligible vapour pressure, no complexity while handling and a higher rate of reactions (Wasserscheid & Keim, 2000). 1-hydroxyhexyl-3-methylimidazolium hexafluorophosphate (HOHxMIm.PF_6) was specially designed and successfully demonstrated as a PTC and a reaction media in heterogeneous glycosidation reactions (Kumar, Talisman, Bukhari, Razzaghy & Malhotra, 2011). Yadav et. al. (2010) used different phosphonium based catalysts, such as, trihexyl(tetradecyl)phosphonium chloride (THTDPC), trihexyl(tetradecyl)phosphonium bromide (THTDPB), trihexyl(tetradecyl)phosphoniumdecanoate (THTDPD), and trihexyl(tetradecyl)phosphoniumhexafluorophosphate (THTDPH) for o-alkylation of 2-napthol to synthesize benzyl 2-napthyl ether and very good conversion and 100% selectivity were found.

The G-L PTC was not found very feasible because the process needs higher temperatures to obtain gaseous anions to carry out the reactions and it can be achieved only in gas-mass spectrophotometer conditions (Tundo, Moraglio, & Trotta, 1989).

There is a scarcity of literature available in the field of L-L-S PTC. A few researchers published papers on the synthesis of fine chemicals using L-L-S PTC. In fact L-L-S PTC is advantageous over L-L PTC process as (i) recovery and reusability of the catalyst is very easy; (ii) it is cheaper than other catalysts; (iii) it is readily available.

Benzoic anhydride was prepared from benzoyl chloride and sodium benzoate with the use of clay-supported quaternary ammonium salts as a PTC at 30 °C under L-L-S PTC, and product selectivity was found to be 100% (Yadav & Naik, 2000). Synthesis of (phenoxy)chlorocyclotriphosphazene was reported from the substitution reaction of hexachlorocyclotriphosphazene using self-prepared poly(styrene-co-chloromethylstyrene) resin as a triphase catalyst (Wu & Wang, 2003). Satrio et. al. (2000) synthesized octyl acetate from different octyl halides using nucleophilic substitution reaction and

tributylmethylammonium chloride as a triphase catalyst. A rigorous kinetic model was also developed based on the Langmuir-Hinshelwood and Eley-Rideal mechanism.

2.3.2 Modeling of multiphase reactions

The role of developing kinetic models is to understand and describe chemical processes such as organic synthesis, microorganism growth, food decomposition, and the complex chemistry of biological systems. The kinetic models can also be useful in the design and modification of chemical reactors to get optimized product yield. Many researchers have developed kinetic models for multiphase reactions (Brahmayya & Wang, 2014; Naik & Doraiswamy, 1997; Wang, Brahmayya, & Hsieh, 2015; Yang, Wu, & Li, 2000). Yadav & Naik, (2001) successfully developed a kinetic model and validated it for thealkoxylation of p-chloronitrobenzene under L-L-L phase transfer catalysis. The same work was carried out for O-alkylation of vanillin with benzyl chloride under tri-liquid phase transfer catalysis (Yadav & Lande, 2005).

2.4 Conclusion

In the literature review, many ways to capture and utilize H_2S were cited. Use of aqueous alkanolamines to absorb H_2S was found to be the most efficient method for H_2S removal, and so in the present work, MEA and MDEA, the two mostly used industrial alkanolamines, were used to absorb H_2S.

There is very less work published on the utilization of H_2S-rich alkanolamine to produce value-added fine chemicals. DBDS is a very useful chemical compound and havingvery diversified applications in the field of organic synthesis. There is no published work on the synthesis of DBDS by utilizing H_2S-rich MEA using solid PTC under L-L-S PTC condition. The major advantage of solid PTC is the feasibility of reusability. In the present work, H_2S-rich MEA was utilized to produce DBDS by reacting it with organic reactant benzyl chloride (BC) using amberlite IR-400 as a solid catalyst under L-L-S PTC condition.

DBS is also very important chemical compound and its applications have already been discussed in Section 2.3 of this chapter. Its synthesis has been done using many ways, and many PTCs were used in the process, but the use of phosphonium based

catalyst as a PTC was not found in the literature. TBPB was found to be a very efficient PTC in a few articles. We have successfully synthesized DBS using TBPB as a PTC under L-L PTC by utilizing H_2S-rich MDEA.

ILs has much application as a replacement of many organic solvents and as a very efficient PTC. A huge amount of literature is available on the use of ILs as a PTC and the same has been already discussed earlier. But utilization of H_2S-rich ethanolamine for the synthesis of thioethers is untouched till now. We have synthesized DBS with 100% selectivity with the use of THTDPC as a PTC under L-L PTC conditions.

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Chapter 3

Experimental

This chapter describes a methodology for experiment work which includes details of chemicals used, experimental setup, preparation of different reagents and the analytical procedure.

3.1 Chemicals

Toluene (≥ 99%), potassium iodide (KI), potassium iodate (KIO_3), starch powder, sodium thiosulfate ($Na_2S_2O_3$) and 98% pure sulfuric acid (H_2SO_4) were purchased from Rankem Ltd. Tetrabutylphosphonium bromide (TBPB) and Trihexyltetradecylphosphonium chloride were obtained from Sigma-Aldrich Pvt. Ltd., India. Monoethanolamine (≥98%) was obtained from Merck Ltd., India. and methyldiethanolamine synthesis grade were procured from Sigma-Aldrich Pvt Ltd., India Synthesis grade benzyl chloride (≥99%), Sodium hydroxide (NaOH) pellets and ferrous sulfide sticks (FeS) were obtained from Merck Ltd., India.

3.2 Preparationof H_2S-rich aqueous alkanolamines

The making of H_2S-rich alkanolamines was done in the laboratory using Kipps's apparatus (Figure 3.1). H_2S was generated from the reaction of ferrous sulfide sticks and sulfuric acid, and it was absorbed in a 250 ml standard gas bubbler containing 30-35 wt% aqueous alkanolamine. The overall reaction can be written as,

$$Fes + H_2SO_4 \rightarrow H_2S + FeSO_4 \text{ (Exothermic)}$$

Since, the above-mentioned reaction is exothermic in nature (Kohl & Nielsen, 1997), the bubbler having aqueous alkanolamine was kept in an ice bath to avoid oxidation and formation of sulfide and disulfide. At regular time interval, samples were withdrawn to evaluate the sulfide concentration with the help of iodometric titration method (Scott, 1966).

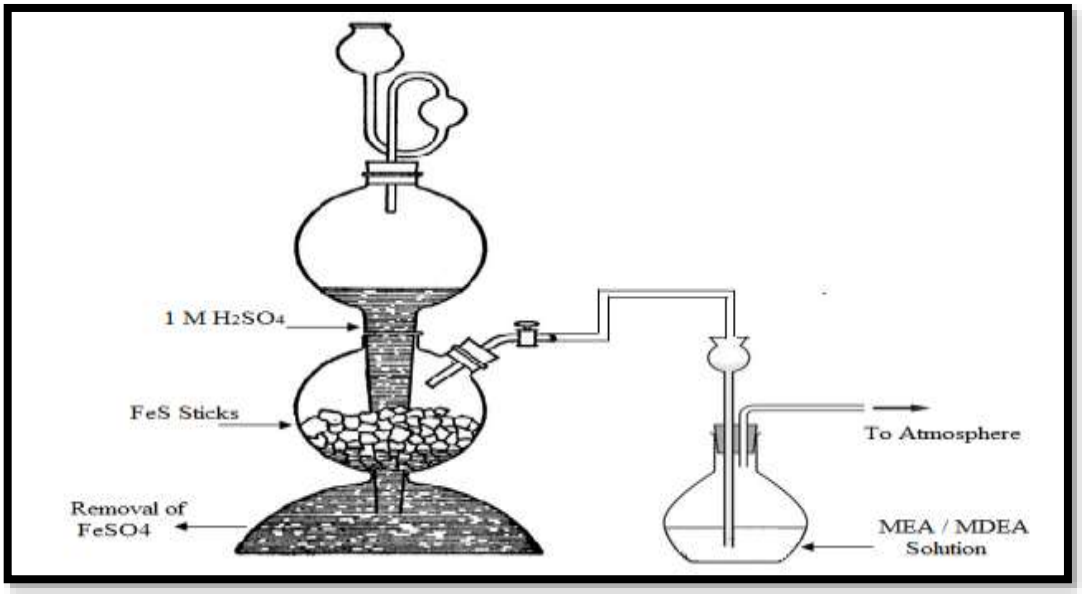

Figure 3.1: H_2S absorption in aqueous alkanolamine solution (Kipps's apparatus)

3.3 Iodometric titration method

The initial concentration of sulfide in H_2S-rich alkanolamine was obtained using iodometric titration method as given below:

- 1 litter of 0.025 M KIO_3 solution was prepared.
- 1 litter of 0.1 M sodium thiosulfate solution was prepared. Few drops of chloroform or little amount of sodium carbonate was added to the solution to keep the concentration unchanged.
- Thiosulfate solution standardization: potassium iodide (KI) was weighed upto 1 g and dissolved in the solution of 25 mL of 0.025M KIO_3. Then 3.0 mL of 1 M sulfuric acid was added to the solution. The thiosulfate solution was used for the titration of the solution till the color turned into pale yellow from brown. Again the solution was made up to 200 ml and 2 cm^3 of starch solution was added. The titration was unremitted till the color altered into colorless from blue. The involved chemical reactions in the procedure are given below.

$$KIO_3 + 5KI + H_2SO_4 \leftrightarrow 3I_2 + 3K_2SO_4 + 3H_2O$$

$$2Na_2S_2O_3 + I_2 \leftrightarrow Na_2S_4O_6 + 2NaI$$

Thus, 1 mole of potassium iodate (KIO_3) ≡ 3×2 mole of sodium thiosulfate ($Na_2S_2O_3$).

$$\therefore \text{Thiosulfate Solution Strenth } (S_{th}) = \frac{6 \times \text{Volume } (KIO_3) \text{ X Strenth } (KIO_3)}{\text{Volume (ConsumedThiosulfate)}}$$

- **Finding of sulfide concentration:** The sulfide concentration can be determined using an oxidation process in a basic medium with potassium iodate. 15 mL of 0.025 M KIO_3 solution was filled in the conical flask and 10 mL of sulfide solution containing approximately 2.5 mg of sulfide was added along with 10 mL of 10M NaOH solution. The mixture was heated to boil for 10 minutes and then cooled. In the cooled solution, then 20 mL of 4M H_2SO_4 solution and 5 mL of KI solution were added. Using a standard solution of 0.1M $Na_2S_2O_3$, titration of the liberated iodine was done to get the reading which is equal to the unused KIO_3. The KIO_3 in the basic medium oxidizes sulfide into sulfate according to the reaction mentioned below. For sulfide solution having an adequately high concentration of sulfide, appropriate dilution was made prior to implementation of the procedure mentioned above.

$$4IO_3^- + 6OH^- + S^{2-} \rightarrow 4SO_4^{2-} + 4I^- + 6H_2O$$

$$4 \text{ moles of liberated iodine} (IO_3^-) = 3 \text{ moles of sulfide } (S^{2-})$$

$$\text{so, the Concentration of } H_2S = \left[15 \times S_{KIO_3} - \frac{V_{th} X S_{th}}{6}\right] \times \frac{3}{4} \times \frac{N_{dl}}{10}$$

Where, S_{KIO_3} = KIO_3Strength

V_{th}= Thiosulfate volume

S_{th}= Thiosulfate Strength

N_{dl}= Number of times of dilution

3.4 Apparatus and equipment setup

All the experiments were performed in an assembly of fully baffled thermostated three-necked mechanically agitated batch reactor having the capacity of 250 cm^3 with a stirrer having six blades of around 2.0 cm diameter, and the speed of agitation can be

controlled manually. The height of impeller was maintained approximately 1.5 cm from the bottom of the reactor, and the complete assembly was dipped in a water bath. The schematic diagram of the experimental setup is as shown in Figure 3.2.

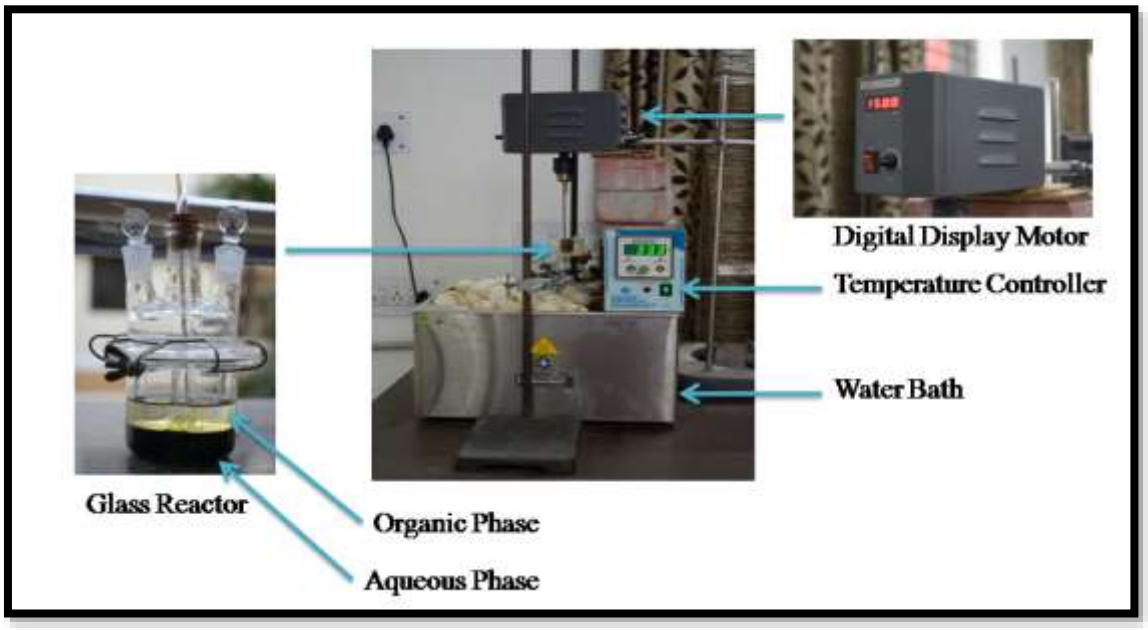

Figure 3.2: Schematic diagram of experimental setup

3.5 Experimental procedure

In every experimental run, 50 cm^3 of the known sulfide concentration aqueous phase was fed into the reactor and kept well agitated until the temperature reaches the set point. Then, the same quantity of the organic phase containing known concentration of organic reactant with solvent and PTC was fed into the reactor. The stirring of the reaction mixture was then carried out at a uniform speed. Approximately 0.5 cm^3 sample from the organic phase was taken at a planned interval of time after stopping the stirring and allowing the phases to get settled down.

3.6 Analysis of organic phase

In present work, quantification was done using GC-FID (Agilent GC 7890B) equipped with a capillary column (DB-5MS, 2 m x 3mm) and a flame ionization detector. The product identification was done by GC-MS (Agilent 5977A).

3.6.1 Identification with GCMS

A known amount of organic sample was injected into the column using a micro syringe fitted with an auto sampler. The sample travels through the column with the carrier gas helium. The compounds present were identified by GCMS. A capillary column is used in the GCMS for the separation of molecules present in the sample mixture and then the mass spectrometer capture, ionize, accelerate, deflect and detect the molecule separately. The different molecular weight of the different compound is given in the spectra, and DBS was identified as molecular weight 214 in and DBDS as 246. A detailed programme followed for the identification in GCMS is given below:

MS Program

Inlet conditions. Heater = 300 ^{0}C, Purge Flow = 3ml/min, Pressure = 11.724 psi (split mode)

Column specifications. Agilent DB-5ms, Pressure = 8.2317 psi, Flow = 1 ml/min, Holdup Time = 1.365 min

Oven condition. Initial Temperature = 60 ^{0}C, Maximum temperature = 300 ^{0}C

	Rate (^{0}C/min)	**Value (^{0}C)**	**Holdup Time (min)**	**Retention Time (min)**
Initial		60	0.25	0.25
Ramp 1	100	150	0	1.15
Ramp 2	50	300	5	9.15

3.6.2 Quantification with GC-FID

A gas chromatograph equipped with flame ionization detector is a chemical analysis instrument for separating and detecting chemicals in a sample mixture. In a GC analysis, a known volume of liquid sample is injected using a micro syringe into the head of the capillary column. In the present analysis nitrogen was used as a carrier gas which sweeps the analyte molecules through the column and the molecules got adsorbed by fillings present in the column called stationary phase. Every molecule has a different progression rate and leaves the column at different time that is called the retention time of

that molecule. Leaving molecules from the column are detected by a flame ionization detector (FID). The FID detects ions which form as a result of combustion of an organic compound by hydrogen flame. The concentration of the organic compound is proportional to the number of ions formed, and this theory was used quantification of the organic phase. The detailed program followed for the quantification using GC-FID is mentioned below:

FID Program

Inlet Condition. Heater = 200 ^{0}C, Pressure = 15.345 psi, Purge Flow = 3ml/min

Column Condition. Agilent DB-5ms, Pressure = 15.345 psi, Flow = 1.5 ml/min, Holdup Time = 1.427 min

Oven Condition. Initial temperature = 60^{0}C, Maximum temperature = 300^{0}C

	Rate (^{0}C/min)	**Value (^{0}C)**	**Holdup Time (min)**	**Retention Time (min)**
Initial		50	0	0
Ramp 1	30	170	0	4
Ramp 2	50	260	0	5.8
Ramp 3	10	280	4.2	12

Detector. Heater = 300^{0}C, H_2 Flow = 30 ml/min, Air Flow = 400 ml/min, Column Flow (N_2) = 15 ml/min, Make up Flow (N_2) = 25 ml/min.

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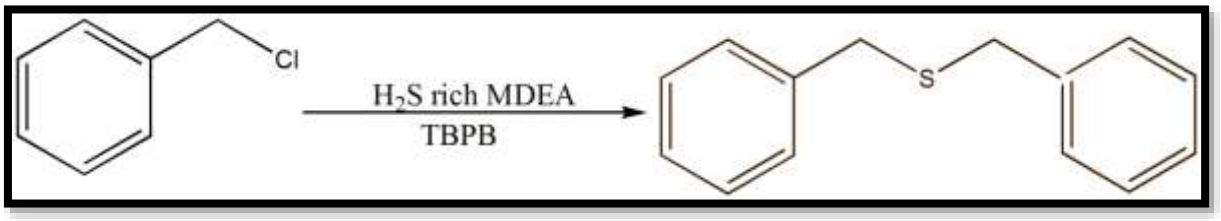
Chapter 4

Synthesis of Dibenzyl Sulfide using H_2S-Rich Aqueous Methyldiethanolamine under Liquid-Liquid Phase Transfer Catalysis

This chapter deals with the detailed kinetic investigation for the selective synthesis of dibenzyl sulphide (DBS) from the reaction of benzyl chloride (BC) and H_2S-rich aqueous methyldiethanolamine (MDEA) under liquid-liquid phase transfer catalysis (L-L PTC). The investigation includes the effect of different parametric on BC conversion and DBS selectivity, mechanistic investigation and statistical modeling. Effect of temperature, catalyst loading, BC/sulfide mole ratio, initial sulfide concentration and MDEA concentration on BC conversion and DBS selectivity were investigated under parametric study.

4.1 Introduction

In the present study, DBS was synthesized selectively from the reaction of BC and aqueous H_2S-MDEA under L-L PTC using TBPB as a PTC. DBS and BM were the only product detected by gas-liquid chromatography (GLC) after the completion of the reaction. The detailed commercial importance of DBS is discussed in Chapter 2. Moreover, there is a possibility of formation of benzyl alcohol and n-benzyl MDEA by alkaline hydrolysis and chlorine atom substitution respectively, but none of them was detected in GLC analysis after the course of the reaction. The overall reaction can be represented by Scheme 4.1.



Scheme 4.1: Overall reaction

Parametric studies have been performed to observe the effect of different parameters such as agitation speed, temperature, catalyst concentration, BC concentration, sulfide concentration and MDEA concentration on BC conversion and DBS selectivity and also a suitable mechanism is proposed to explain the course of the reaction.

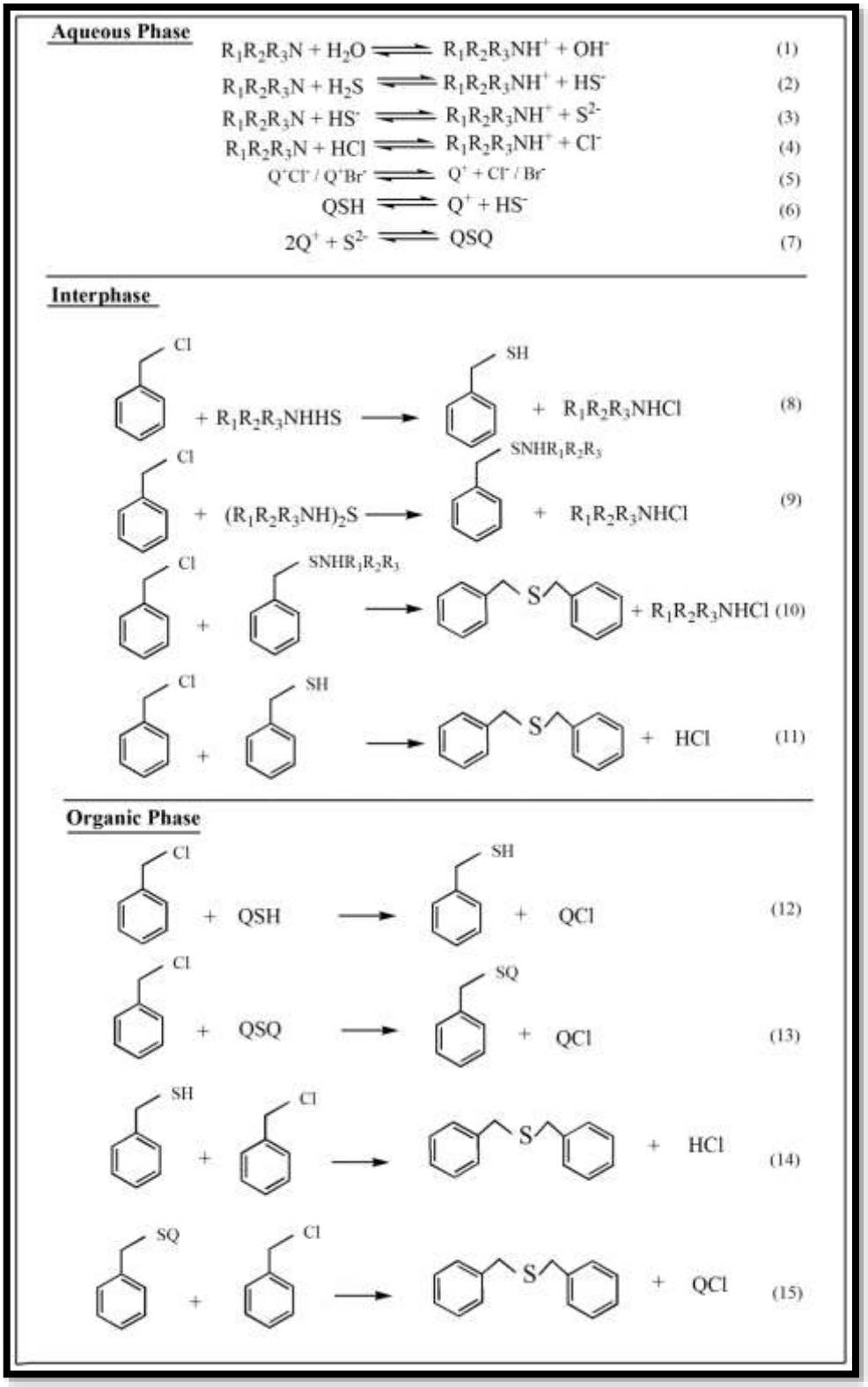
4.2 Result and discussion

4.2.1 Proposed mechanism of synthesis of dibenzyl sulfide under L-L PTC

Depending on the lipophilicity of the PTC employed, PTC function in two different mechanistic routes- extraction mechanism and interfacial mechanism. If the PTC is not highly lipophilic, extraction mechanism is useful to explain the course of the reaction, and if the catalyst is highly lipophilic one then it will remain in the organic phase and anion exchange reaction will take place only at the interphase.

TBPB, like its nitrogen analog TBAB, has properties like distribution coefficient, extraction constant, etc. in the same order and magnitude (Wu & Tseng, 2002) and therefore like TBAB (Sen, Pradhan, & Patwardhan, 2011), TBPB can be expected to show similar lipophilicity and partitioning property in a two-phase system. In the present work, the liquid–liquid system involving TBPB can, therefore, be explained by Stark's extraction mechanism. Generally aqueous phase reactions are faster as compare to organic phase reactions, so an ionic equilibrium exists in aqueous phase among the tertiary alkanolamine $R_1R_2R_3N$ (MDEA), H_2O and dissolved H_2S, which results in formation of three active inorganic nucleophiles namely hydroxide (OH^-), hydrosulfide (HS^-) and sulfide (S^{2-}) as represented by Eqs.(1)-(4) in Scheme 4.2. These ions present in the aqueous phase are capable of reacting with quaternary phosphonium cation Q^+ $[(C_4H_9)_4P^+]$ to produce QSQ, QSH and QOH ion pairs in the aqueous phase.

Since, the partition coefficient of TBPB is good (Alexander, 2003), the ion pairs formed in the aqueous phase can easily migrate into the organic phase where they react with BC to give desired product DBS. Since the product DBS was identified without catalyst as well, the reaction product is expected to form via both non-catalytic and catalytic pathways as shown in Scheme 4.2.



Scheme 4.2. Proposed mechanism of synthesis of DBS by H_2S-laden MDEA under L-L PTC

4.2.1.1 Non-catalytic contribution

In the absence of a catalyst, the reaction is expected to occur only at the liquid-liquid interface. In this case, methyldiethanolamine hydrosulfide ($R_1R_2R_3NHHS$) and sulfide $(R_1R_2R_3NH)_2S$, both forms in an aqueous phase and reacts with BC at the organic-aqueous interface to yield DBS and BM. Eqs. (8)- (11) in Scheme 4.2 represents the non-catalytic reactions occur at the interface. Since the nucleophilic substitution reactions are generally of 2nd order, the reaction between BC and $(R_1R_2R_3NH)_2S$ are assumed to form an intermediate $C_6H_5CH_2SNHR_1R_2R_3$ (Eq. (9)) which further react with BC to yield DBS. BM again expected to react with BC to give high DBS selectivity (Eq. (11)).

4.2.1.2 Catalytic Contribution

Both sulfide and hydrosulfide ions present in the aqueous phase exchange ions with Q^+X^- to form active catalysts ion pairs $Q^+S^{2-}Q^+$ and Q^+SH^- and crosses the interphase and transfers into an organic phase and react with BC to produce DBS and BM respectively as shown in Eqs. (12) - (15). DBS is also expected to form via reaction of BM with BC.

4.2.3 Parametric Study

4.2.3.1 Effect of stirring speed

The experiment was performed at different stirring speed ranges from 1000 to 2500 rpm in order investigate the mass transfer resistance on the rate of reaction. The rate of reaction was found almost same in every experiment of stirring speed variation as shown in Fig. 4.1. Therefore, we can say that with an increase in stirring speed there is no mass transfer effect on the rate of reaction and reaction can be considered as completely kinetically controlled. It is clear from the Fig. 4.2 that stirring speed does not give any effect on the final conversion of BC and the selectivity of DBS. Thus, further synthesis was carried out at 1500 rpm to ensure the negligible effect of mass transfer resistance. In the absence of a catalyst, the rate of reaction is very low. Therefore, further experiments have been performed in the presence of catalyst only.

4.2.3.2 Effect of catalyst concentration

The reaction was carried out in both, the absence and presence of TBPB. In the absence of a catalyst the BC conversion reached to 45% which was found to increase drastically to 88% in the presence of a catalyst. The experiments were performed with a different concentration of catalyst ranges between 0.05 to 0.15 kmol/m^3 of the organic phase. The enhancement factor of up to six times was observed with the maximum catalyst loading performed as shown in Table 4.1.

Table 4.1: Effect of catalyst loading on Initial reaction rate

Concentration of TBPB (kmol/m^3 org phase)	**Initial reaction rate (kmol/m^3s) at 5% Conversion**	**Enhancement Factor**
0.00	5.00×10^{-4}	1.00
0.05	1.20×10^{-3}	2.26
0.10	2.10×10^{-3}	3.77
0.15	2.80×10^{-3}	5.28

[a]All other conditions are same as Fig.4.3.

Selectivity of DBS increased drastically from 40% in the absence of a catalyst to 85% in the presence of 0.15 kmol/m^3 of catalyst (Fig. 4.3(b)). So it can be concluded that at high catalyst concentration, active catalyst intermediate (QSQ) is a dominating species responsible for DBS synthesis, giving high DBS selectivity.

In order to calculate the order of reaction with respect to TBPB catalyst, the natural logarithm of the initial reaction rate of different catalyst concentration was plotted against the natural logarithm of TBPB concentration (Fig. 4.4). The order of reaction, obtained from the slope of the plot, was 0.77 which can be considered to be 1st order with respect to catalyst concentration.

4.2.3.3 Effect of temperature

The effect of temperature on conversion of BC and selectivity of DBS was studied here. The temperature was varied from 303-333 K keeping other experimental conditions constant. The expected nature of increased BC conversion with an increase in temperature

was noticed according to transition state theory. Fig 4.5(a) and (b) shows an increase in BC conversion without a significant increase in DBS selectivity.

The initial reaction rate was calculated to obtain Arrhenius plot of ln(initial rate) vs. 1/T (K^{-1}) at various temperature (Fig. 4.6). The activation energy, calculated from the slope of Arrhenius plot, is found to be 70.67 kJ/mol which again supports in favor of kinetically controlled reaction.

4.2.3.4 Effect of benzyl chloride concentration

The influence of the reactant BC on BC conversion and DBS selectivity was observed by varying the BC/sulfide mole ratio in the range 1.16–2.89 as shown in Fig. 4.7(a) and (b) respectively. The decrease in BC conversion was noticed with gradual increase in BC/sulfide mole ratio due to unavailability of sufficient aqueous S^{2-} and HS^{-} anions in the aqueous phase.

An opposite pattern to BC conversion was observed in the case of DBS selectivity as it increased suddenly at high BC/sulfide mole ratio (Fig. 4.7(b)). Increased DBS selectivity was caused by the conversion of BM to DBS in the presence of excess BC. In present work, to get appreciable conversion as well as selectivity, BC/sulfide mole ratio of 1.73 was considered as optimum for further study.

In order to find the order of reaction with respect to BC concentration, a graph of ln(initial rate) was plotted against ln(concentration of BC) (Fig. 4.8). The order of the reaction was calculated from the slop of the straight line as 0.73. Hence, the reaction can be considered as first order w.r.t. BC concentration.

4.2.3.5 Effect of sulfide concentration

The effect of sulfide concentration on the conversion of BC conversion was investigated, and concentration of MDEA kept constant. To study the effect of sulfide concentration experiment was carried out with four different sulfide concentrations from 1.25 to 2 $kmol/m^3$. At 1.25 $kmol/m^3$ sulfide concentration, BC conversion was found as 82%, and it reaches to 100% at 2.0 $kmol/m^3$ sulfide concentration after the completion of the reaction. The conversion of BC increases because with an increase in sulfide concentration availability of active sites also increases.

In the case of selectivity, opposite trend was observed as DBS selectivity decreases with increase in sulfide concentration. At 1.25 kmol/m^3 sulfide concentration, DBS selectivity was 76%, and it decreases to 47% at sulfide concentration of 2 kmol/m^3 after the completion of the reaction. The reason for the decrease in the DBS selectivity is the formation of more HS^- ions which produce more QSH active sites.

In order to find the order of reaction with respect to sulfide concentration, a graph of ln(initial rate) was plotted against ln(sulfide concentration) (Fig. 4.10). The order of the reaction was calculated from the slope of the straight line as 0.98. Hence, the reaction can be considered as first order w.r.t. sulfide.

4.2.3.6 Effect of MDEA concentration

Increase in both BC conversion (Fig. 4.11(a)) and DBS selectivity (Fig. 11(b)) were observed with increasing MDEA concentration. Even though MDEA does not influence the reaction directly, it pushes the MDEA-H_2S-H_2O equilibrium towards more ionization of H_2S to S^{2-} and thereby enhances both BC conversion and DBS selectivity. From Scheme 4.2, it is clear that S^{2-} anions are responsible for the formation of QSQ catalyst intermediates which further reacts with 2 moles of BC to give DBS. So high concentration of sulfide anions (S^{2-}) not only increases conversion of BC but also increases DBS selectivity.

4.3 Kinetic modeling

4.3.1 Development of kinetic model

A kinetic model for the synthesis of DBS has been developed with the assumption that in the presence of PTC, the non-catalytic contribution towards the formation of DBS is negligible in comparison to catalytic one. So, the rate of the overall reaction depends on the concentration of the reactant (C_r), sulfide (C_s) and catalyst (C_c) raised to the orders as found experimentally earlier. Therefore, the rate of reaction can be expressed as follows:

$$-r = k_{app} C_r^{0.73} C_s^{0.98} C_C^{0.77} \quad (16)$$

The overall mass balance for sulfide can be obtained from overall reaction for the formation of DBS, and is given by Eq. (17).

$$C_s = C_{s_0} - 1/2f(C_{r_0} - C_r) \quad (17)$$

Where, C_{r_0} and C_{s_0} are initial concentration of reactant and sulfide respectively and f is the ratio of the volume of the organic phase to that of aqueous phase.

A nonlinear regression algorithm has been used for the estimation of parameters and to estimate the optimum value of (k_{app}) by minimizing the objective function (E) as given by the Eq. (18)

$$E = \sum_{i=1}^{n}[\{(-r_A)_{pred}\}_i - \{(-r_A)_{expt}\}_i]^2 \quad (18)$$

The optimum values of rate constant (k_{app}) for DBS synthesis at different temperatures were estimated and tabulated in Table 4.2.

The activation energy of the reaction was evaluated from the slope of the Arrhenius plot of ln (k_{app}) against 1/T and found to be 33.59 kJ/mol (Fig. 4.12).

Table 4.2: Rate Constants of the Model

Temperature(K)	**Rate constant (with catalyst)** $k_{app}((kmol/m^3)^{-4}.s^{-1})$
303	2.00×10^{-4}
313	1.80×10^{-3}
323	2.30×10^{-3}
333	4.70×10^{-3}

The conversions of BC calculated on the basis of rate constants given in Table 4.2 were compared with the experimentally obtained BC conversion and is demonstrated in Fig. 4.13. A very good correlation was therefore observed, and that validate the assumption used in developing the kinetic model.

4.4 Identification and Quantification

The product was identified using GC-MS (Agilent 5977A). The temperature programming followed is mentioned in Chapter 3. DBS was successfully identified from the analysis and the graph obtained from GC-MS is represented in Fig. 4.14.

The quantification of the product was done using GC-FID (Agilent GC 7890B). The temperature programming followed is mentioned in Chapter 3. Each sample was analyzed using GC-FID, and the kinetic study was performed. As an example, initial and final graphs of one parameter are represented in Fig. 4.15 and 4.16.

4.5 Conclusion

A viable reaction methodology has been developed for the synthesis of dibenzyl sulfide from H_2S-rich methyldiethanolamie under liquid-liquid phase transfer catalysis. The used PTC, TBAB was found to be effective in selective synthesis of the thioethers. The blend of high thioethers yield and selectivity, milder operating conditions and a potentially great substitution to energy- and cost-expensive Claus process makes this method economically and environmentally attractive. The proposed mechanism has been successfully explained the course of the reaction. The activation energy for the catalytic reaction has been found to be 70.67 kJ//mol. An empirical kinetic model was also developed based on the detailed kinetic study and validated successfully against the experimental data.

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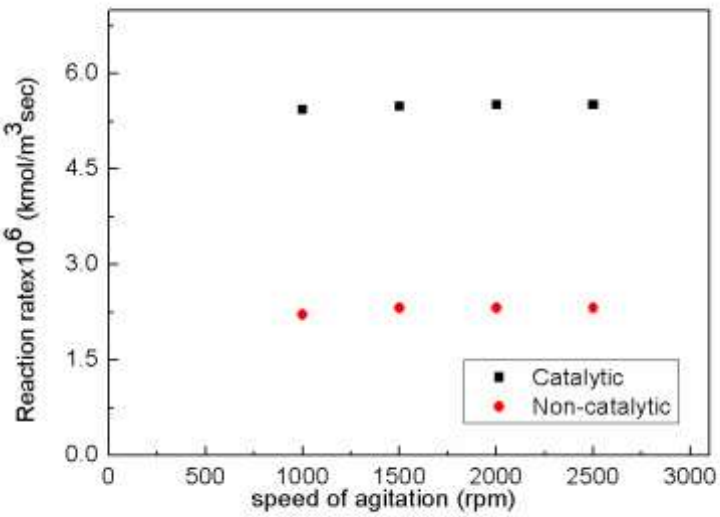


Figure 4.1: Effect of stirring speed on the reaction rate. Operating conditions: volume of aqueous and organic phase = 5.0× $10^{-5}$$m^3$each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; concentration of sulfide = 1.5 kmol/m^3; concentration of catalyst = 0.15 kmol/m^3 org. phase; temperature = 323 K; MDEA concentration = 3.05 kmol/m^3.

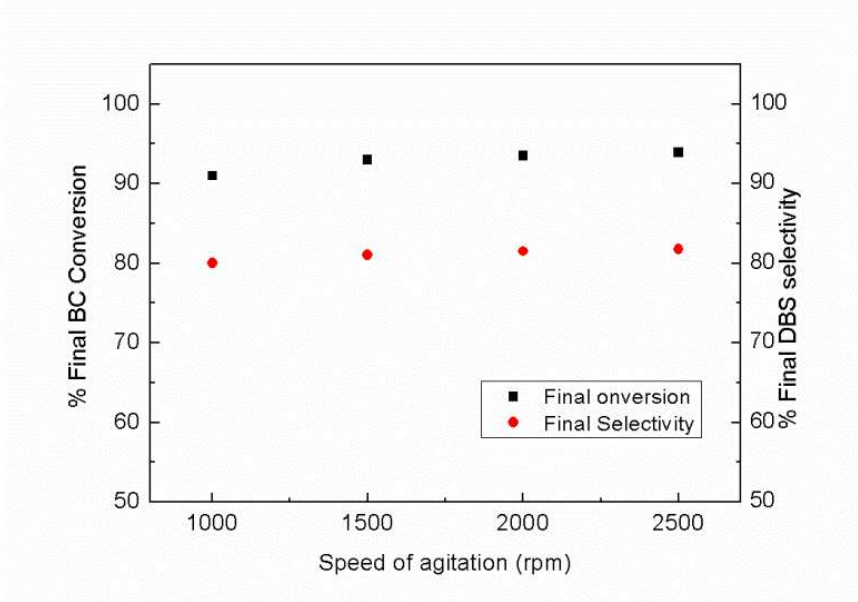
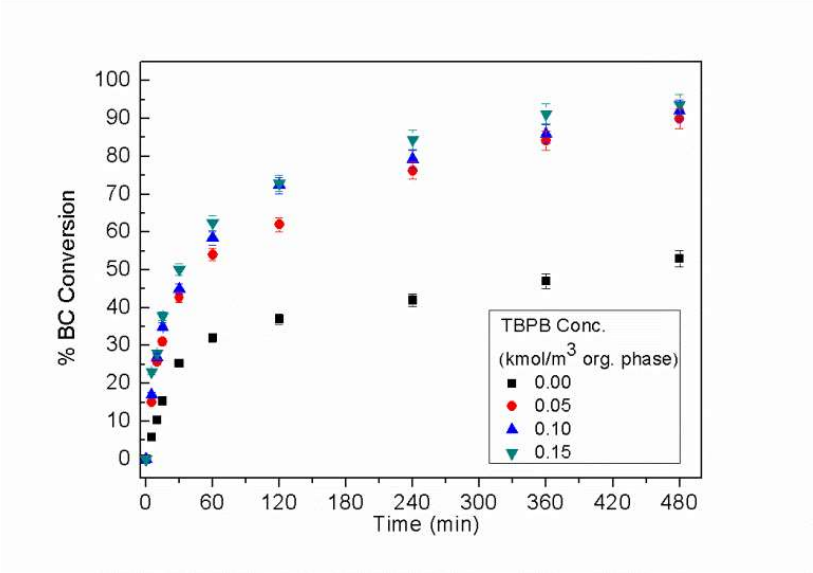
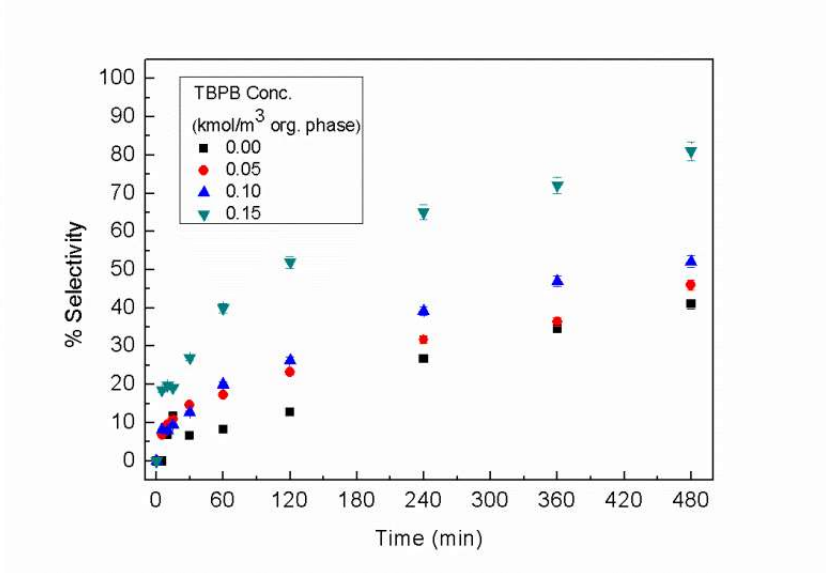


Figure 4.2: Effect of stirring speed on conversion of BC and selectivity of DBS. All other conditions are same as Fig. 4.1.



(a)



(b)

Figure 4.3: Effect of catalyst concentration on (a) BC conversion (b) DBS selectivity. Operating conditions: Volume of aqueous and organic phase = 5.0×10^{-5} m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; concentration of sulfide = 1.5 kmol/m^3; temperature = 323 K; MDEA concentration = 3.05 kmol/m^3.

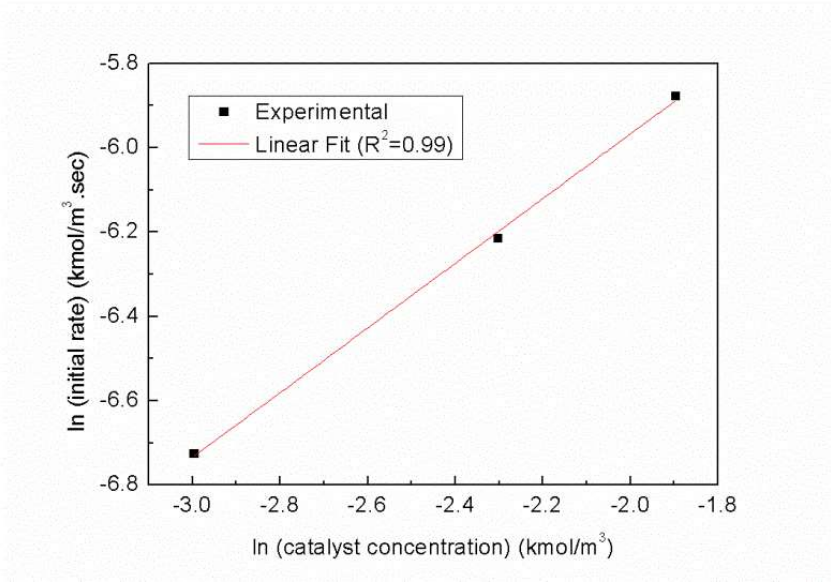
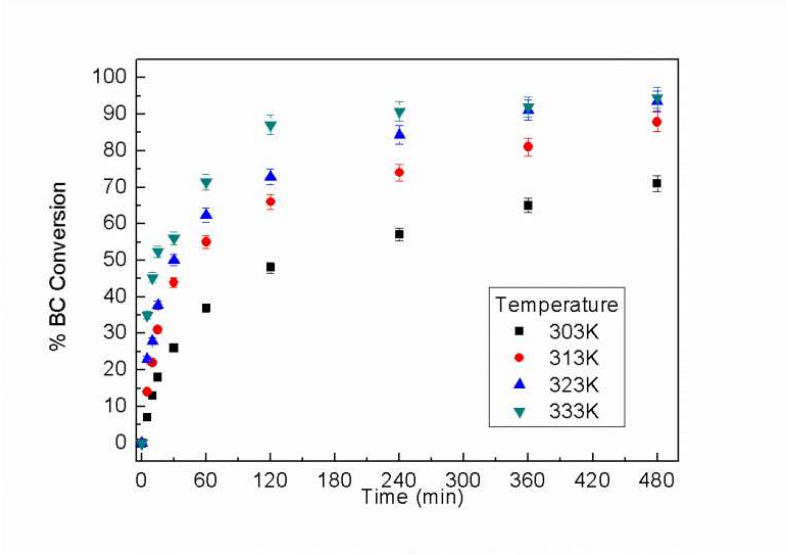
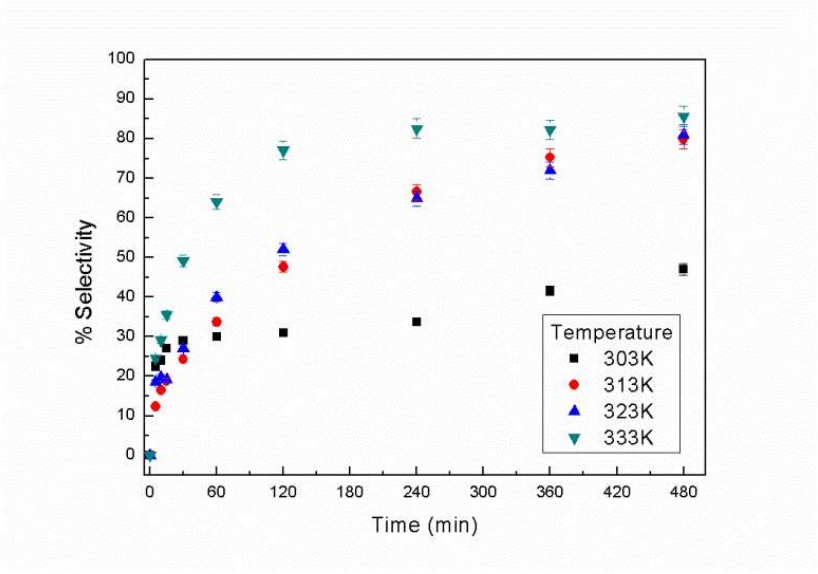


Figure 4.4: Plot of ln (Initial Reaction Rate) vs. ln(catalyst concentration). All other conditions are same as Fig. 4.3.



(a)



(b)

Figure 4.5: Effect of temperature on (a) BC conversion (b) DBS selectivity. Operating conditions: volume of aqueous and organic phase = $5.0\times\ 10^{-5}$m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; concentration of sulfide = 1.5 kmol/m^3; concentration of catalyst = 0.15 kmol/m^3 org. phase; MDEA concentration = 3.05 kmol/m^3.

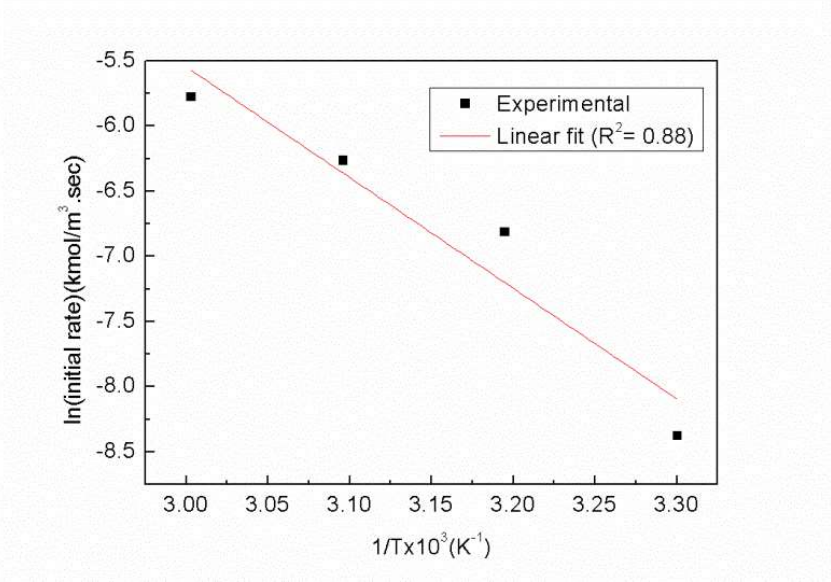
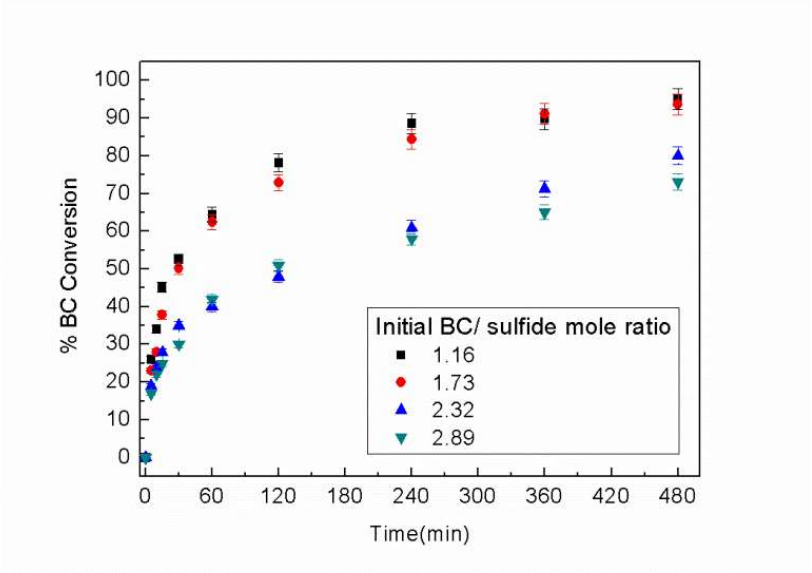
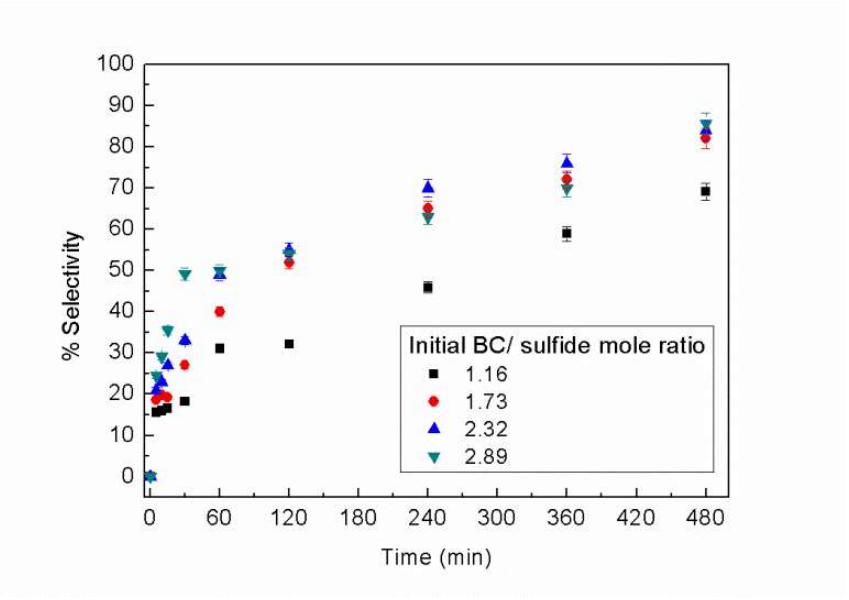


Figure 4.6: Arrhenius plot of ln (initial reaction rate) vs. 1/T. All other conditions are same as Fig.4.5.



(a)



(b)

Figure 4.7: Effect of BC concentration on (a) BC conversion (b) DBS selectivity. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5} m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of sulfide = 1.5 kmol/m^3; concentration of catalyst = 0.15 kmol/m^3 org. phase; temperature = 323 K; MDEA concentration = 3.05 kmol/m^3.

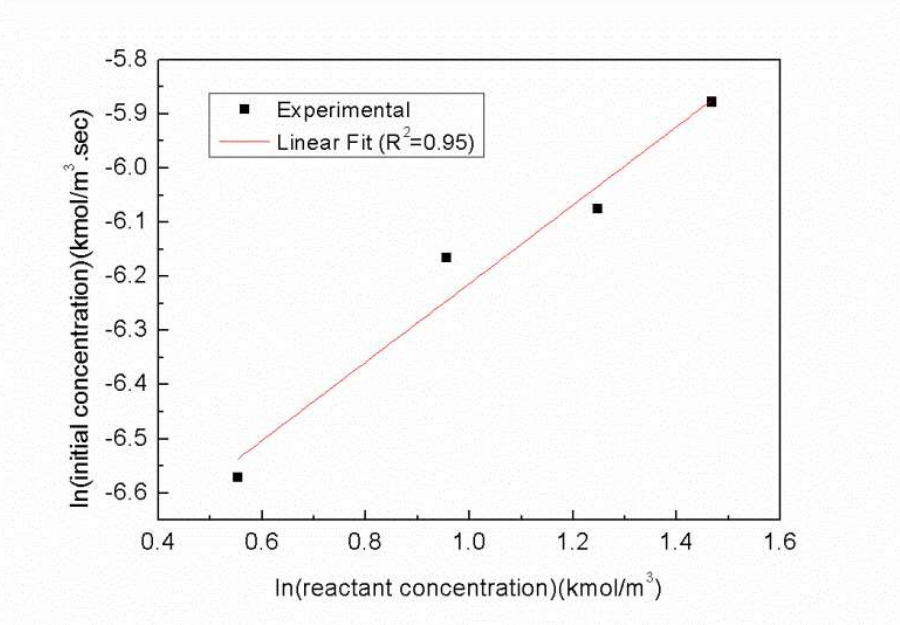
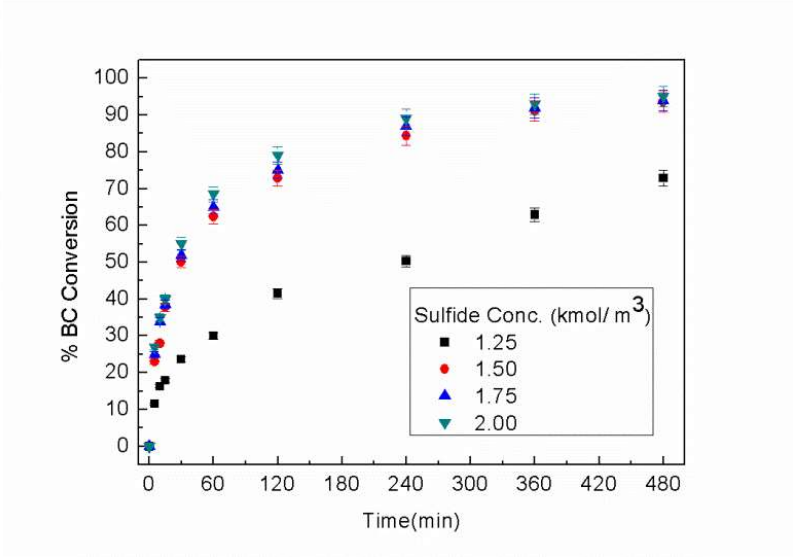
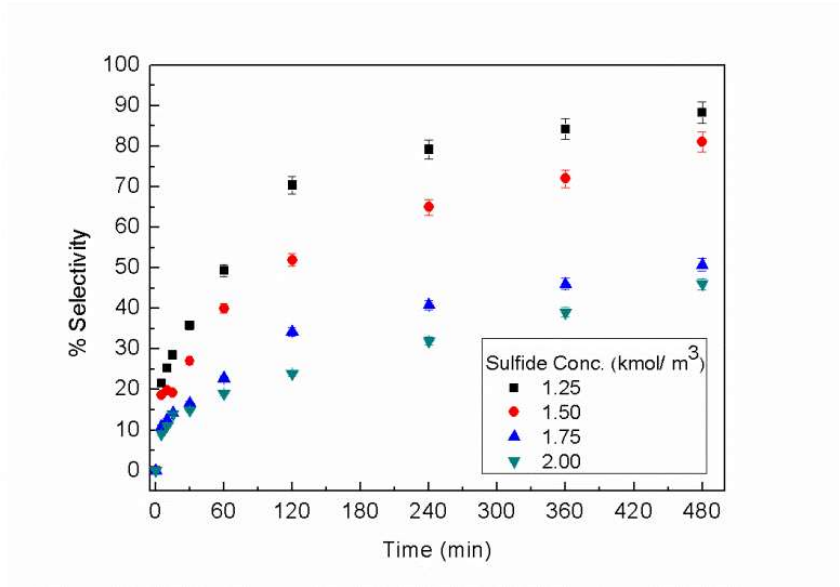


Figure 4.8: Plot of ln(initial reaction rate) vs. In (reactant conc.). All other conditions are same as Fig. 4.7.



(a)



(b)

Figure 4.9: Effect of Sulfide concentration on (a) BC conversion (b) DBS selectivity. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5} m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of catalyst = 0.15 kmol/m^3 org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; temperature = 323 K; MDEA concentration = 3.05 kmol/m^3.

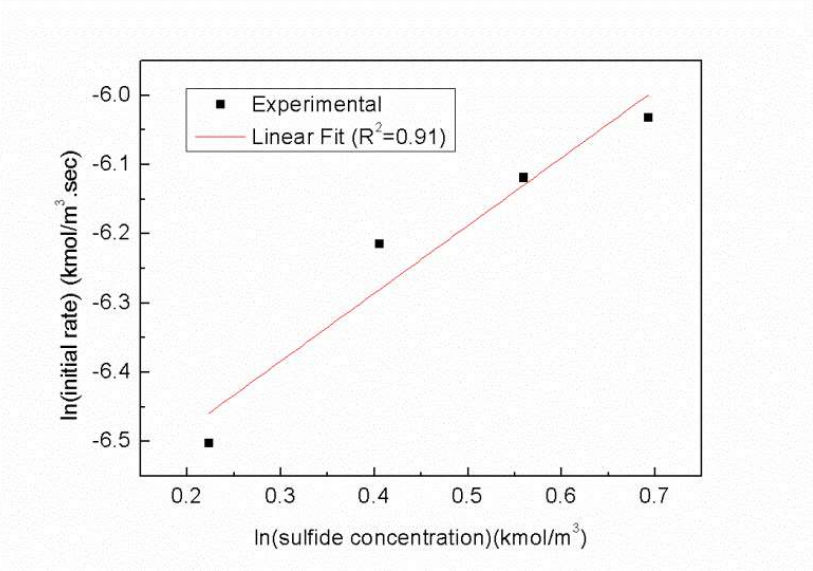
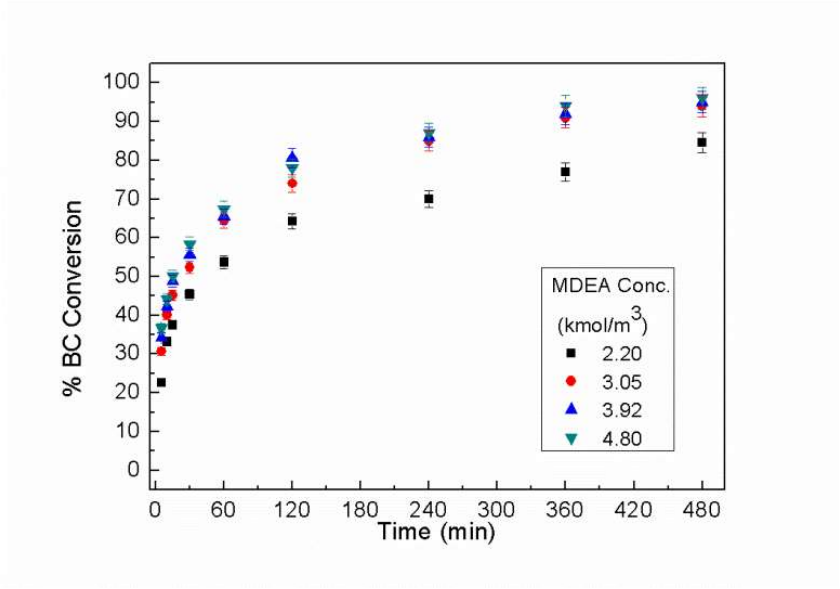
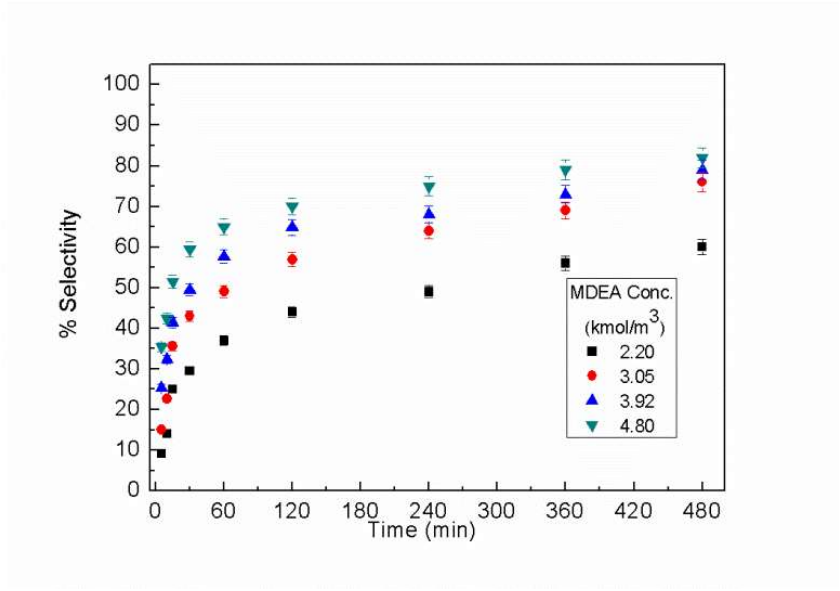


Figure 4.10: Plot of ln (initial reaction rate) vs. ln(sulfide conc.). All other conditions are same as Fig. 4.9.



(a)



(b)

Figure 4.11: Effect of MDEA concentration on (a) BC conversion (b) DBS selectivity. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5} m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of catalyst = 0.15 kmol/m^3 org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; temperature = 323 K; concentration of sulfide = 1.5 kmol/m^3.

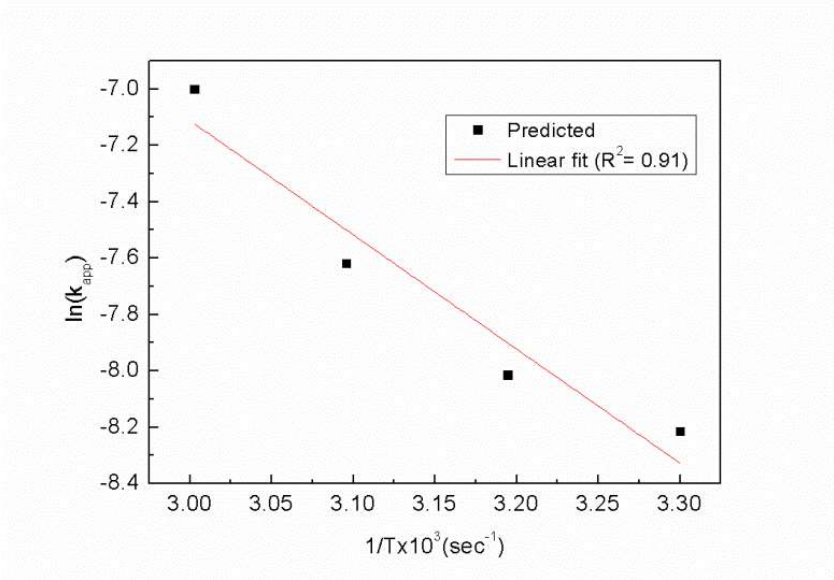


Figure 12: Arrhenius plot of ln(k_{app}) vs. 1/T

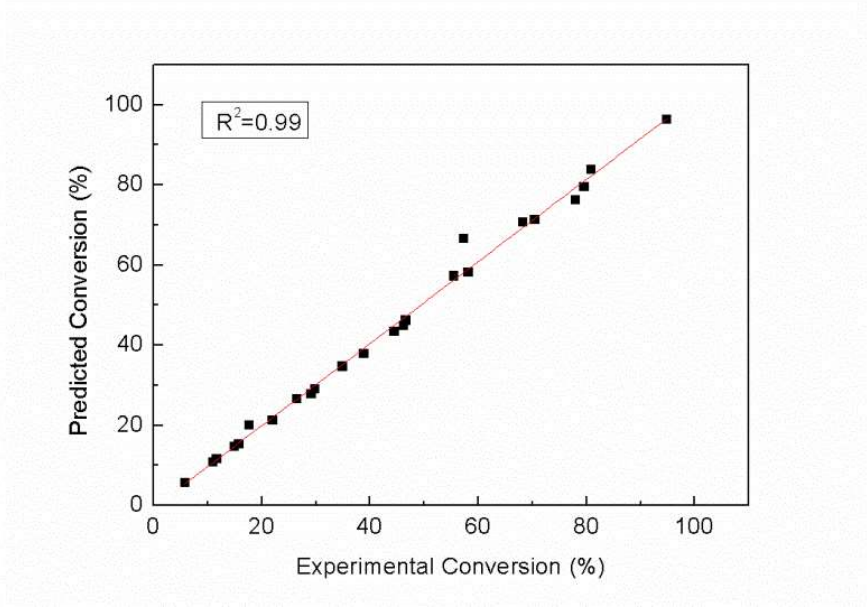


Figure 4.13: Comparison of calculated and experimental conversion of BC.

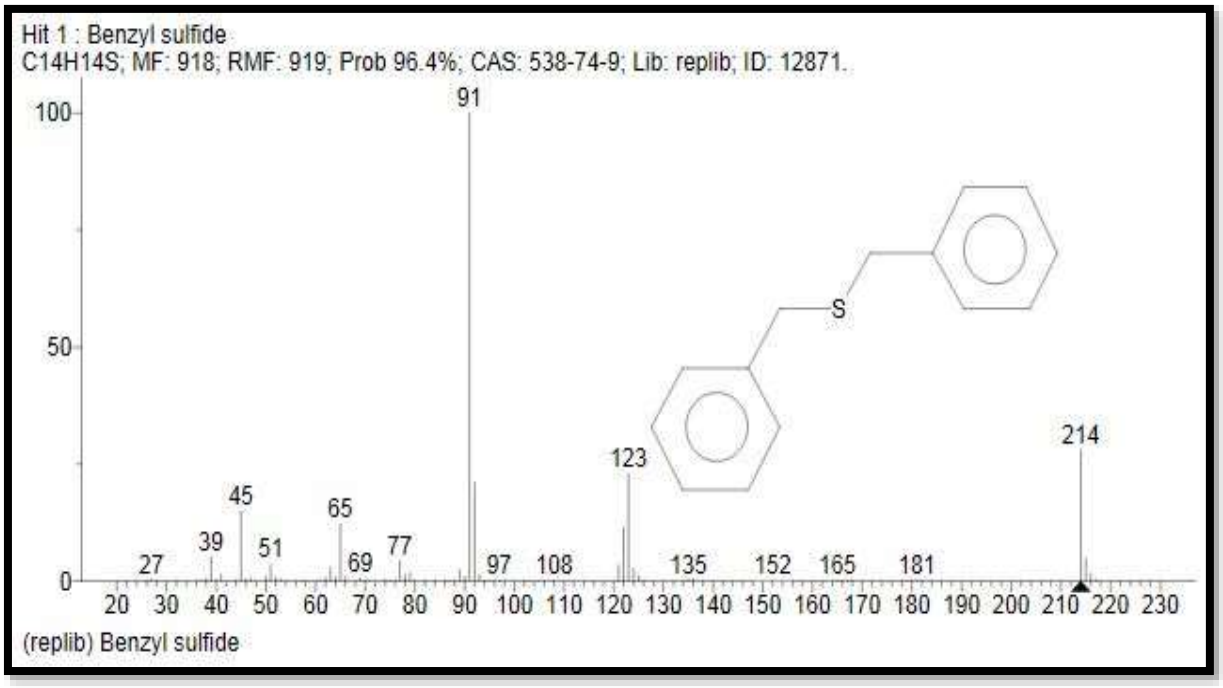


Figure 4.14: MS spectra for DBS

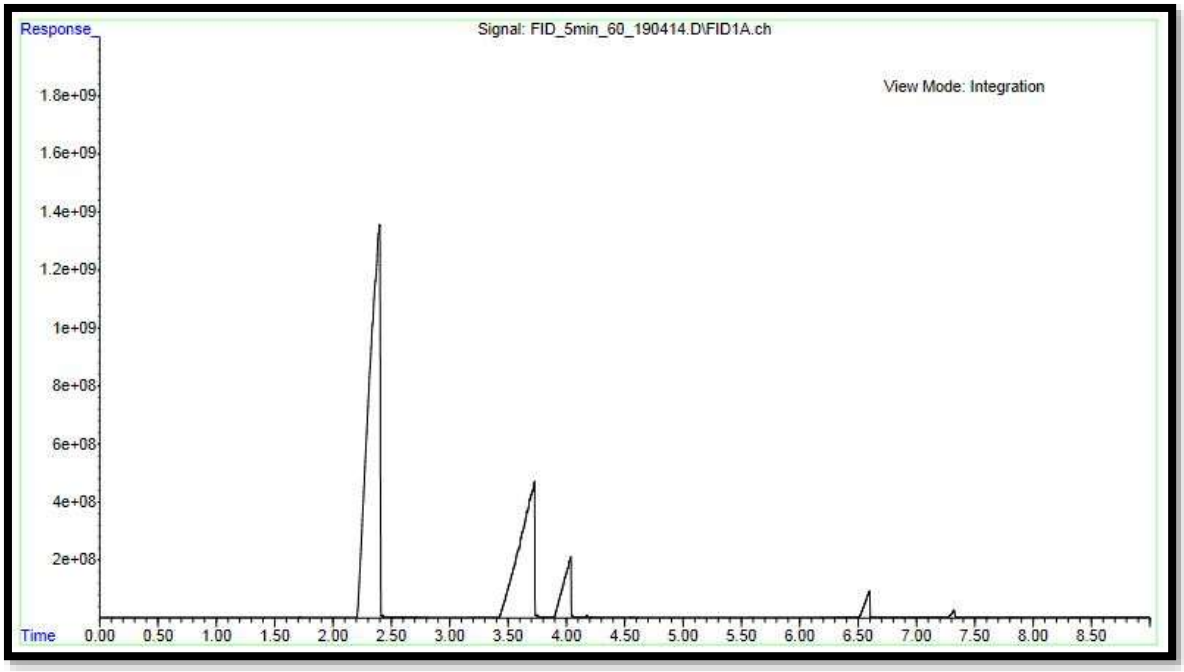


Figure 4.15: GLC chromatogram for DBS after 5 min of reaction time in presence of TBPB

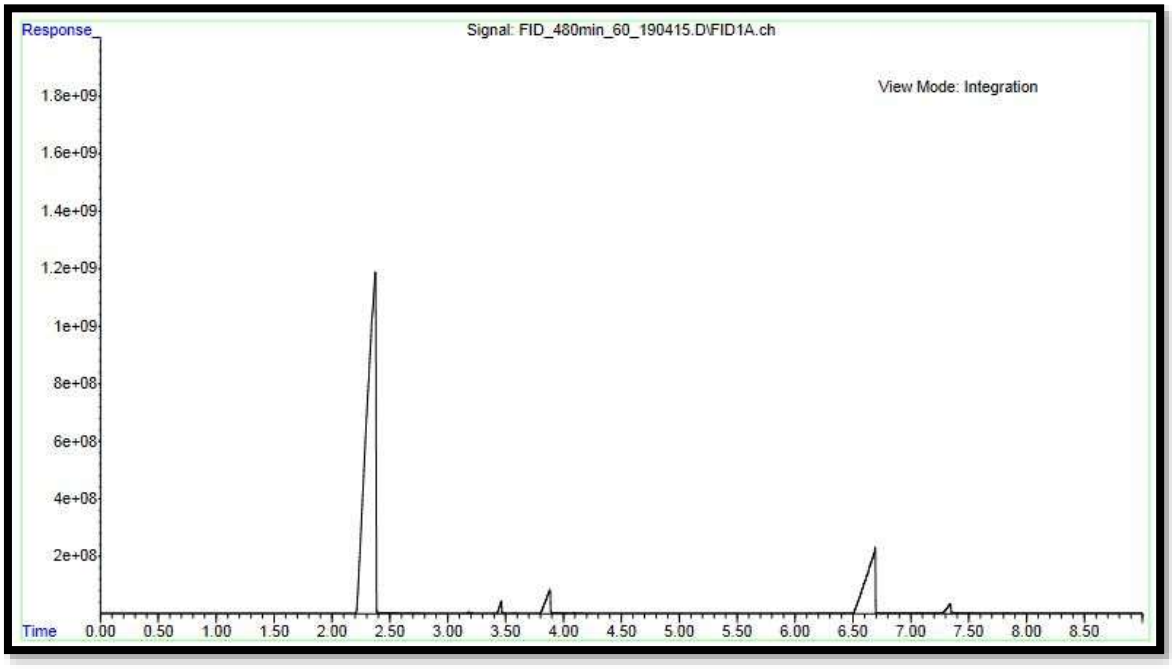


Figure 4.16: GLC chromatogram for DBS after 480 min of reaction time in presence of TBPB

Chapter 5

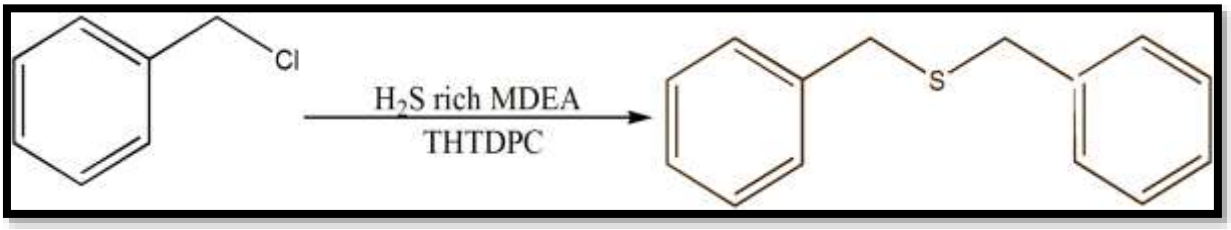
Synthesis of Dibenzyl Sulfide using

Ionic Liquids as a Phase Transfer Catalyst

This chapter deals with the detailed kinetic investigation and the selective synthesis of dibenzyl sulfide (DBS) from the reaction of aqueous H_2S-rich methyldiethanolamine (MDEA) with benzyl chloride (BC) under liquid-liquid phase transfer catalysis (L-L PTC). This investigation includes the effect of different parametric on BC conversion and DBS selectivity, mechanistic investigation and kinetic modeling. Effect of temperature, catalyst loading, BC/sulfide mole ratio, and initial sulfide concentration on the conversion of BC and DBS selectivity were investigated under parametric study.

5.1 Introduction

This study dealt with the selective synthesis of DBS from the reaction of BC and aqueous H_2S-MDEA using THTDPC as a PTC under L-L PTC. After the completion of the reaction, DBS was the only identified product by gas-liquid chromatography (GLC). The detailed commercial importance of DBS is discussed in Chapter 2. This process can be considered as the replacement of Claus process as the H_2S-MDEA can be directly used for the synthesis of fine chemicals. The reaction in the present study was carried out in both the conditions, in the absence and presence of a catalyst in a batch reactor. The overall reaction is represented by Scheme 5.1.



Scheme 5.1: Overall reaction

The purpose of the parametric studies is to observe the effect of different parameters, such as agitation speed, temperature, concentration of BC, catalyst concentration and sulfide concentration on BC conversion and DBS selectivity. Also a suitable mechanism was proposed to understand the pathway of the reaction.

5.2 Result and discussion

5.2.1Parametric study

5.2.1.1 Effect of stirring speed

The experiment was carried out at different stirring speed ranges from 1000 to 2500 rpm in order investigate the mass transfer resistance on the rate of reaction. The rate of reaction was found almost same in every experiment of stirring speed variation as shown in Fig. 5.1. Therefore, we can say that with an increase in stirring speed there is no effect on the rate of reaction and reaction can be considered as completely kinetically controlled. Thus, the further synthesis was carried out at 1500 rpm to ensure no effect of mass transfer resistance. In the case of no catalyst, the reaction rate was very low, so the further experiments were carried out only in the presence of the catalyst.

5.2.1.2 Effect of Catalyst Concentration

To study the effect of catalyst concentration, experiments were carried out in the absence of a catalyst and with different concentrations of the catalyst. In the absence of a catalyst, the BC conversion reached to 49% which was increased drastically to 97% in the presence of a catalyst (Fig. 5.2(a)). The experiments were performed with a different concentration of catalyst ranges between 0.01 to 0.03 kmol/m^3 of the organic phase. The enhancement factor of up to eleven times was observed with the maximum catalyst loading performed as shown in Table 5.1.

Selectivity of DBS increased drastically from 41% in the absence of a catalyst to 100% in the presence of 0.15 kmol/m^3 of catalyst (Fig. 5.2(b)). So it can be concluded that at high catalyst concentration, more active catalyst intermediate (QSQ) and (QSH) forms that reacts with BC to synthesize DBS.

Table 5.1: Effect of catalyst loading on Initial reaction rate

Concentration of THTDPC (kmol/m^3 org phase)	**Initial reaction rate (kmol/m^{3}s)**	**Enhancement Factor**
0.00	5.10×10^{-4}	1.00
0.05	3.90×10^{-3}	7.65
0.10	5.20×10^{-3}	10.20
0.15	5.90×10^{-3}	11.60

All other conditions are same as Fig.2.

5.2.1.3 Effect of Temperature

To study the temperature effect on BC conversion and DBS selectivity, experiments were carried out at four different temperature, 303-333 K with an increase of 10 K and the other experiments conditions were kept constant. It was shown in Fig. 5.3 (a) that the BC conversion increases with temperature increase and this nature of graph also satisfies the transition state theory. Fig. 5.3 (b) shows that with an increase in temperature there is no significant increase in selectivity of DBS.

The initial reaction rates of all experiments performed at different temperature were calculated, and an Arrhenius plot was drawn between ln(initial reaction rate) and 1/T (K^{-1}) shown in Fig. 5.4. The activation energy was calculated from the slope of the straight line in the Arrhenius plot. The obtained activation energy is 16.88 kJ/mol.

5.2.1.4 Effect of benzyl chloride concentration

The influence of the reactant BC on conversion of BC and DBS selectivity was observed by varying the BC/sulfide mole ratio in the range 1.74 – 3.47 as shown in Fig. 5.5 (a) and (b) respectively. The aqueous S^{2-} and HS^- anions in the aqueous phase are limited, and consumption of complete BC in the case of high BC/sulphide mole ratio is not possible, and so, a decrease in BC conversion was noticed with gradual increase in BC/sulfide mole ratio.

An opposite pattern to BC conversion was observed in the case of DBS selectivity as it increased suddenly at high BC/sulfide mole ratio (Fig. 5.4(b)). In present work, 2.60 BC/sulfide mole ratio was considered as an optimum value for further study to get appreciable conversion as well as selectivity.

5.2.1.5 Effect of sulfide concentration

The influence of the concentration of sulfide on the conversion of BC was investigated, and concentration of MDEA was kept constant. To study the effect of sulfide concentration, experimental work was done with four different sulfide concentrations from 1.50 to 2.25 kmol/m^3. At 1.5 kmol/m^3 sulfide concentration, BC conversion was found as 97%, and it reaches to 99% at 2.25 kmol/m^3 sulfide concentration after the completion of reaction (Fig. 5.6(a)). The conversion of BC increases because with an increase in sulfide concentration, availability of active sites QSQ and QSH, also increase.

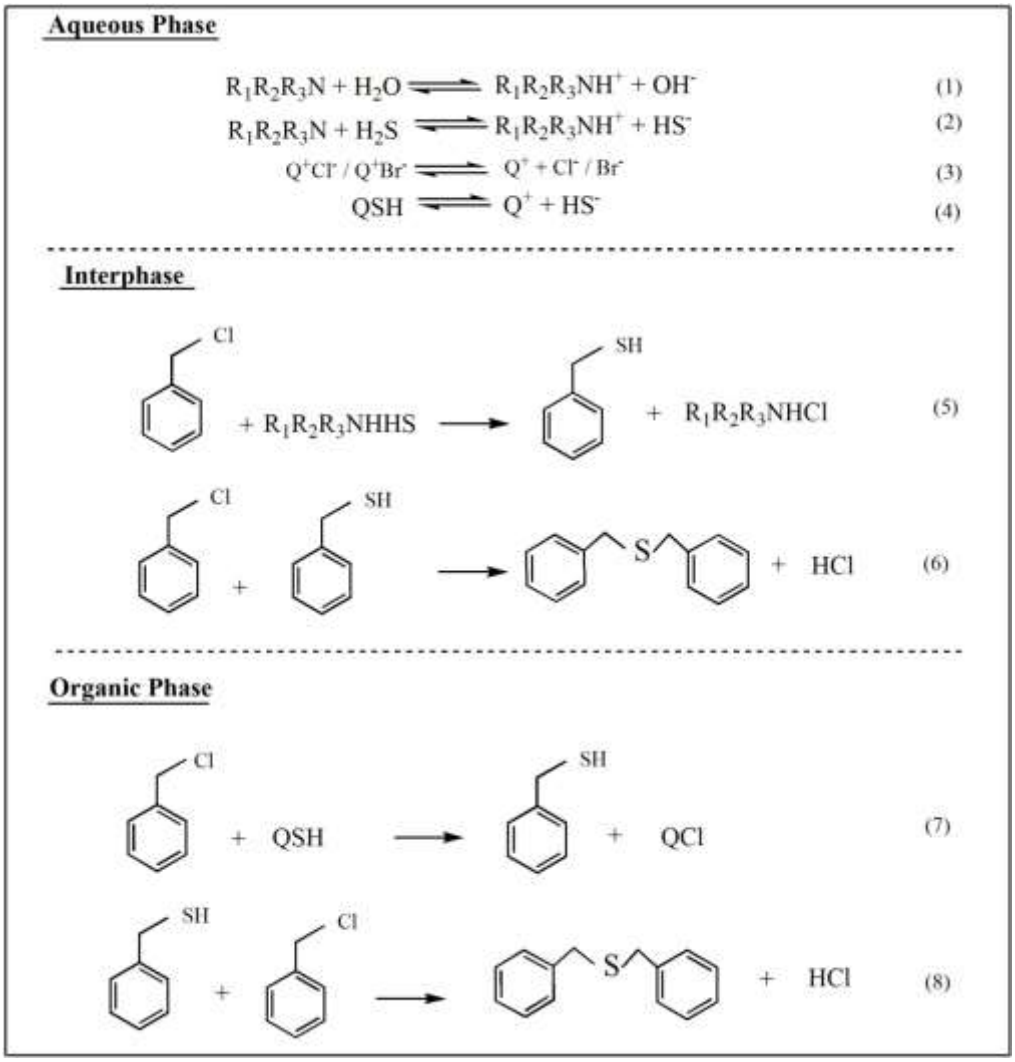
In the case of selectivity of DBS, it decreases with increase in sulfide concentration Fig. 5.6 (b). When the sulfide concentration was 1.5 kmol/m^3, the selectivity of DBS was found to be 100%. The reason for less selectivity of DBS is the high production of QSH active site, which is responsible for the formation of more benzyl mercaptan.

5.3 Proposed mechanism for synthesis of dibenzyl sulfide under L-L PTC

In the present work, THTDPC was used as a PTC that can distribute itself between both the organic and the aqueous phases. Generally reactions in the aqueous phase are faster than the reactions in organic phase, so there is the formation of hydrosulfide (HS^-) and hydroxide (OH^-) (active nucleophiles) in the ionic equilibrium existing among the tertiary alkanolamine $R_1R_2R_3N$ (MDEA), H_2O and dissolved H_2S, as shown in Scheme 5.2 (Eqs.(1)-(4)).

The nucleophiles formed in the aqueous phase reacts with the catalyst cation $[\{CH_3(CH_2)_5\}_3(CH_2)_{13}CH_3P^+]$ termed as (Q) and forms an ion pair QSQ, QSH, and QOH. It is found in the literature that the formation of QSQ is negligible as compare to QSH in the aqueous phase. The ion pair formed in the aqueous phase immediately transfers into

the organic phase and reacts with BC to form BM. BM again reacts with BC to yield the desired product DBS. Eqs. (5) - (6) represents the non-catalytic reactions occur in absence of any catalysts and reaction mechanism in the organic phase and Eqs. (7) – (8) demonstrated the catalytic reactions.



Scheme 5.2. Proposed mechanism of synthesis of DBS by H_2S-laden MDEA under L-L PTC

5.4 Kinetic modeling

5.4.1 Modelling of aqueous phase ionic equilibria

Edwards, et al. (1975), studied the ionic equilibria in the aqueous solutions containing one or more volatile weak electrolytes: NH_3, CO_2, H_2S, SO_2, and HCN and

presented a good thermodynamic frame work for the calculation of vapor-liquid equilibria of weak electrolytes present in the aqueous phase. In the same way, in the present work, an ionic equilibria framework of $R_1R_2R_3N$-H_2O-H_2S in the aqueous phase has been developed. The ionic equilibrium gives species such as R_3N, H_2S, $[R_3NH^+]$, H^+, HS^-, S^{2-} and OH^- in the aqueous phase. The ionic equilibrium is expressed by dissociation constant in terms of their molar concentration in aqueous phase, can be obtained easily from literature (Maity, Sen, & Pradhan, 2009), and represented in the following equations-

$$K_{R_3N} = \frac{[R_3NH^+][OH^-]}{[R_3N]} \quad (7)$$

$$K_{H_2S} = \frac{[HS^-][H^+]}{[H_2S]} \quad (8)$$

$$K_{HS^-} = \frac{[S^{2-}][H^+]}{[HS^-]} \quad (9)$$

The ion product constant of water is given as

$$K_{H_2O} = [OH^-][H^+] \quad (10)$$

To get a concentration of seven species, we need three more equations in addition to above equations. So mass balance and charge balances are taken.

Total MDEA balance in aqueous phase

$$T_{R_3N} = [R_3NH^+] + [R_3N] \quad (11)$$

Total sulfide balance in aqueous phase

$$T_S = [HS^-] + [H_2S] + [S^{2-}] \quad (12)$$

Concentration of charged species in aqueous phase

$$3[R_3NH^+] - 2[H^+] + [S^{2-}] - [OH^-] = 0 \quad (13)$$

In order to find the hydrosulfide and sulfide ion concentration, the seven equations mentioned above having seven unknowns were solved as linear simultaneous algebraic equations using MATLAB and graphs were obtained.

From Fig. 5.7 (a) and (b), we can see that the concentration of hydrosulfide ions (~ 10^{-7}) is more than the sulfide ions (~ 10^{-14}) in the aqueous phase. The values obtained for each anion species is the steady state optimized values. MDEA concentration value is kept constant with varying sulfide concentration, and HS^- anion concentration was found to be much more than S^{2-} anions.

In Fig. 5.8 (a) and (b), the concentration of hydrosulfide ions (~ 10^{-2}) was observed to be more than the sulfide ions (~ 10^{-7}) in the aqueous phase. We can see that the conc. of HS- ions have increased by 10^5 times & that of S^{2-} has increased by 10^7 times. The graphs are nearly linear in nature. It shows that if the concentration of sulfide is low and MDEA concentration is high, a significant chunk (in %) of the reactant gets converted.

In Fig. 5.9, we kept MDEA concentration fixed at 3.5 kmol/m^3 and sulfide concentration varied from 2.1 to 2.25 kmol/m^3. In that case, also we found the same behavior of graph as we found in Fig. 5.7. In all cases, the concentration of HS^- ions is much higher than S^{2-} ions.

These values show the contribution of the aqueous phase in the determination of major product. Also, there is not much driving force to make sulfide ions instead of hydrosulfide anions; hence, the product will be dibenzyl sulfide. In the represented graphs, we have three different scenarios that deal with the contributions of sulfide & hydrosulfide anions.

5.4.2 Modeling of organic phase

Dibenzyl sulfide (RSR) was synthesized from the reaction of benzyl chloride (RCl) and H_2S-rich MDEA. The (QHS) ion pair form in the aqueous phase which crosses the interphase and reaches in the organic phase. The ion pair (QHS) reacts with organic reactant (RCl) and gives the intermediate product (RHS) which instantaneously reacts with (RCl) and converted into the desired product (RSR).

The reaction of substrate (RCl) to yield RSR is divided into two parts as given below:

$$RCl + QHS \xrightarrow{k_{1_{org}}} RHS + QCl \qquad (14)$$

$$RCl + RHS \xrightarrow{k_{2org}} RSR + HCl \quad (15)$$

The ion exchange step in the aqueous phase:

$$[Q^+Cl^-]_{aq} + [HS^-]_{aq} \overset{K_1}{\leftrightarrow} [Q^+HS^-]_{aq} + [Cl^-]_{aq} \quad (16)$$

In the present work, a model has been developed based on the proposed mechanism and the experimental data were used for the validation of the model. The GC analysis shows 100% selectivity for DBS, so we can say that the intermediate product (RHS) completely converts to give desired product, RSR and will not remain in the organic phase.

The ion-exchange equilibrium across the interface can be written in terms of an overall exchange reaction equilibrium constant (K_e), which is also called selectivity equilibrium constant, for exchange of $[Cl^-]_{aq}$ by $[HS^-]_{aq}$ and its transfer to the organic phase, by the following equations:

$$[Q^+Cl^-]_{org} + [HS^-]_{aq} \overset{K_e}{\leftrightarrow} [Q^+HS^-]_{org} + [Cl^-]_{aq} \quad (17)$$

$$K_e = \frac{[Q^+HS^-]_{org}}{[Q^+Cl^-]_{org}} \frac{[Cl^-]_{aq}}{[HS^-]_{aq}} \quad (18)$$

The distribution constants of individual ion-pair and their relationship with K_e and K_1 are given by:

$$K_{QCl} = \frac{[Q^+Cl^-]_{org}}{[Q^+Cl^-]_{aq}} \quad (19)$$

$$K_{QHS} = \frac{[Q^+HS^-]_{org}}{[Q^+HS^-]_{aq}} \quad (20)$$

Substituting Eq. (19) and eq. (20) in Eq. (18)

$$K_e = \frac{K_{QHS}[Q^+HS^-]_{aq}}{K_{QCl}[Q^+Cl^-]_{aq}} \frac{[Cl^-]_{aq}}{[HS^-]_{aq}} = \frac{K_{QHS}}{K_{QCl}} K_1 \quad (21)$$

$$K_e \frac{K_{QCl}}{K_{QHS}} = K_1 \quad (22)$$

Eq. (22) represents the equilibrium constant for the ion exchange reaction in the aqueous phase.

Eq. (14) is the slow reaction and so be the rate determining step while Eq. (15) is fast reaction. From Eq. (14), the rate of reaction is

$$-r_{org} = -\frac{d[RCl]_{org}}{dt} = k_{org}\,[RCL]_{org}\,[Q^+HS^-]_{org} \tag{23}$$

In Eq. (23), the active catalyst concentration term $[Q^+HS^-]_{org}$ needs to be substituted with the known concentration terms from Eq. (18).

$$[Q^+HS^-]_{org} = \frac{K_e[Q^+Cl^-]_{org}[HS^-]_{aq}}{[Cl^-]_{aq}} \tag{24}$$

There are two ion-pairs of catalyst (Q^+HS^-) and (Q^+Cl^-) distributed in aqueous and organic phases. If the total amount of catalyst is N_Q (mol) which is initially added to the reaction mixture, $\emptyset$ is the fraction of the catalyst cation Q^+ distributed in the organic phase and V_{org} is the total volume of the organic phase, then:

$$[Q^+Cl^-]_{org}V_{org} + [Q^+HS^-]_{org}V_{org} = \emptyset N_Q \tag{25}$$

If $V_{aq}$is the total volume of aqueous phase, then:

$$[Q^+Cl^-]_{aq}V_{aq} + [Q^+HS^-]_{aq}V_{aq} = (1-\emptyset)N_Q \tag{26}$$

From Eq. (25),

$$[Q^+HS^-]_{org} = \emptyset\frac{N_Q}{V_{org}} - [Q^+Cl^-]_{org} \tag{27}$$

The total concentration of the catalyst (mol/unit organic phase volume) in organic phase can be defined as:

$$[N_Q]_{org} = \frac{N_Q}{V_{org}} \tag{28}$$

Eq. (20) can be written as:

$$[Q^+HS^-]_{org} = \frac{\emptyset[N_Q]_{org}}{\left(1+\frac{1}{K_e}\frac{[Cl^-]_{aq}}{[HS^-]_{aq}}\right)} \tag{29}$$

The rate of reaction (Eq. 23) can be rewrite using Eq. (29) as:

$$-r_{org} = -\frac{d[RCl]_{org}}{dt} = k_{org}\,[RCL]_{org}\,\frac{\emptyset[N_Q]_{org}}{\left(1+\frac{1}{K_e}\frac{[Cl^-]_{aq}}{[HS^-]_{aq}}\right)} \quad (30)$$

If X_{RCl} is the fractional conversion organic substrate (RCl), then all the concentration terms $[RCl]_{org}$, $[Cl^-]_{aq}$ and $[HS^-]_{aq}$ in Eq. (30) can be substitutes as:

$$\frac{dX_{RCl}}{dt} = k_{org}\,\frac{\emptyset[N_Q]_{org}(1-X_{RCl})}{\left(1+\frac{1}{K_e}\frac{X_{RCl}}{(1-X_{RCl})}\right)} \quad (31)$$

After separation of different variables and integration, Eq. (30) can be represented as:

$$\ln(1-X_{RCl})\,[1-K_e] + \frac{X_{RCl}}{(1-X_{RCl})} = K_e k_{org}\emptyset[N_Q]_{org}t \quad (32)$$

We can rearrange Eq. (32) in the form of straight line equation as given below:

$$\frac{X_{RCl}}{(1-X_{RCl})\ln(1-X_{RCl})} = K_e k_{org}\emptyset[N_Q]_{org}\frac{t}{\ln(1-X_{RCl})} + [K_e - 1] \quad (33)$$

Eq. (33) represents the straight line equation. If we plot $(X_{RCl}/(1-X_{RCl})\ln(1-X_{RCl}))$ against $(t/(\ln(1-X_{RCl}))$, it should give an intercept $[K_e - 1]$ and slope of $K_e k_{org}\emptyset[N_Q]_{org}$ (time-1) and from which the equilibrium constant K_e and the rate constant $k' = k_{org}\emptyset$ can be obtained.

5.5 Validation of the kinetic model

The kinetic model was validated by considering Eq. (27) to be valid at different temperatures. The plot of $(X_{RCl}/(1-X_{RCl})\ln(1-X_{RCl}))$ against $(t/(\ln(1-X_{RCl}))$ is shown in Fig. 5.10 which gives four straight lines with an intercept of $[K_e - 1]$ and slope of $K_e k_{org}\emptyset[N_Q]_{org}$ (time-1). From the numeric value of intercept and slope, we can obtain equilibrium constant K_e and rate constant $k' = k_{org}\emptyset$. Since $\emptyset \cong 1$, so $k' = k_{org}$.

The rate constants were used to derive Arrhenius plot as shown in Fig. 5.11. The activation energy obtained from Arrhenius plot was 42.0 kJ/mol.

5.6 Identification and quantification

The product was identified using GC-MS (Agilent 5977A). The temperature programming followed is mentioned in Chapter 3. DBS was successfully identified from the analysis and the graph obtained from GC-MS is represented in Fig. 5.12.

The quantification of the product was done using GC-FID (Agilent GC 7890B). The temperature programming followed is mentioned in Chapter 3. Each sample was analyzed using GC-FID, and the kinetic study was performed. As an example, initial and final graphs of one parameter are represented in Fig. 5.13 and 5.14.

5.7 Conclusion

The process presented in this chapter can be considered as an economically and environmentally friendly and a worthy alternative to the energy and cost expensive Claus technology. It dealt with the synthesis of selective synthesis of DBS from the reaction of H_2S-rich MDEA with BC in a batch reactor under L-L PTC condition using THTDPC as a PTC. The proposed mechanism has been successfully explained the course of the reaction. The activation energy for the catalytic reaction has been found to be 16.88 kJ//mol and 42.0 kJ//mol from the Arrhenius plot between 1/T and ln of the rate of reaction and rate constant. A mathematical model was developed and validated successfully with the experimental data.

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Edwards, T. J., Newman, J., & Prausnitz, J. M. (1975). Thermodynamics of aqueous solutions containing volatile weak electrolytes. *AIChE Journal*, *21*, 248–25.

Maity, S. K., Sen, S., & Pradhan, N. C. (2009). A new mechanistic model for liquid-liquid phase transfer catalysis: Reaction of benzyl chloride with aqueous ammonium sulfide. *Chemical Engineering Science*, *64*, 4365–4374.

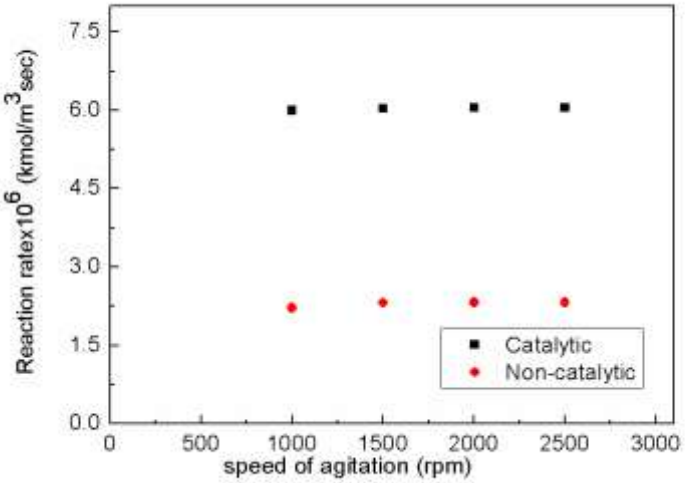
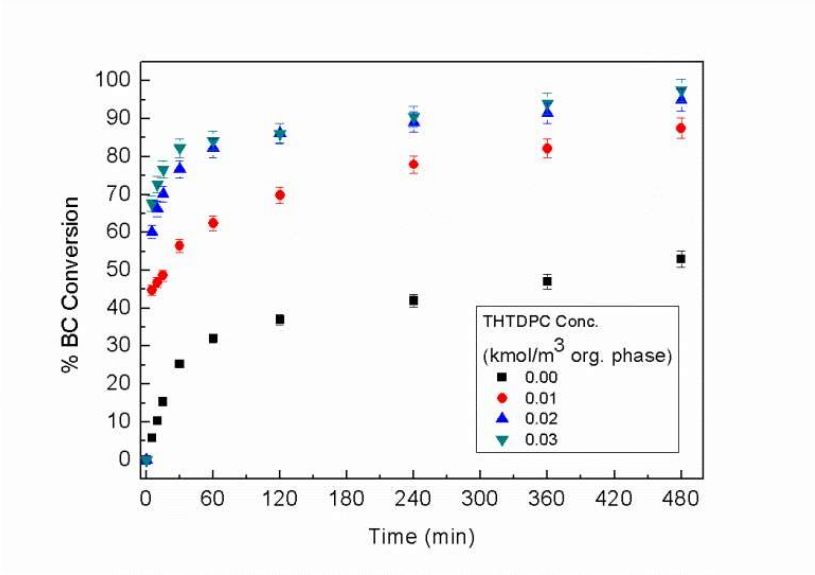
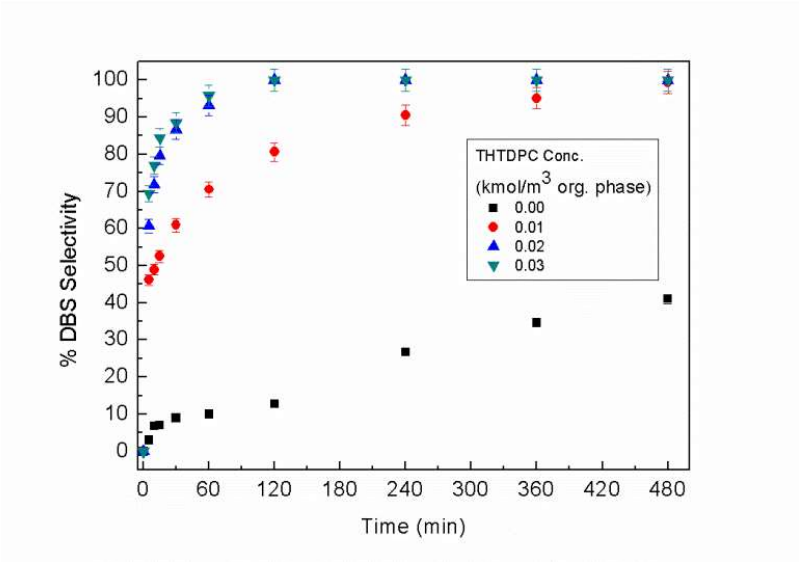


Figure 5.1: Effect of stirring speed on the reaction rate. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5} m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of catalyst = 0.03 kmol/m^3 org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; MDEA conc. = 3.05 kmol/m^3; concentration of sulfide = 1.5 kmol/m^3; temperature = 323 K.

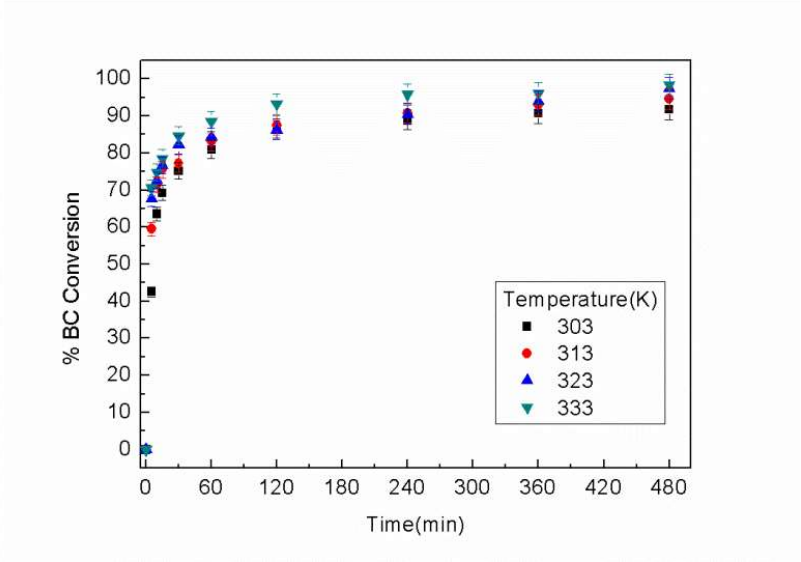


(a)

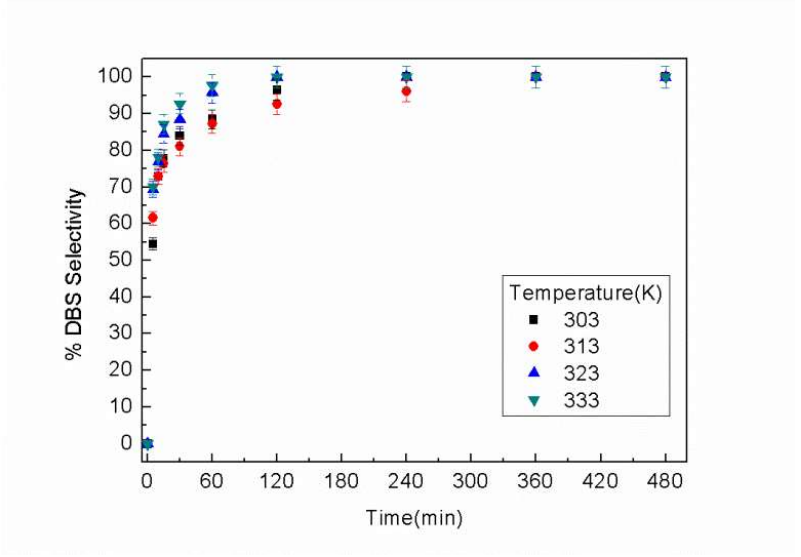


(b)

Figure 5.2: Effect of catalyst loading on (a) BC conversion (b) DBS selectivity. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5} m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; MDEA conc. = 3.05 kmol/m^3; concentration of sulfide = 1.5 kmol/m^3, temperature = 323 K.



(a)



(b)

Figure 5.3: Effect of temperature on (a) BC conversion (b) DBS selectivity. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5}m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of catalyst = 0.03 kmol/m^3 org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; MDEA conc. = 3.05 kmol/m^3; concentration of sulphide = 1.5 kmol/m^3.

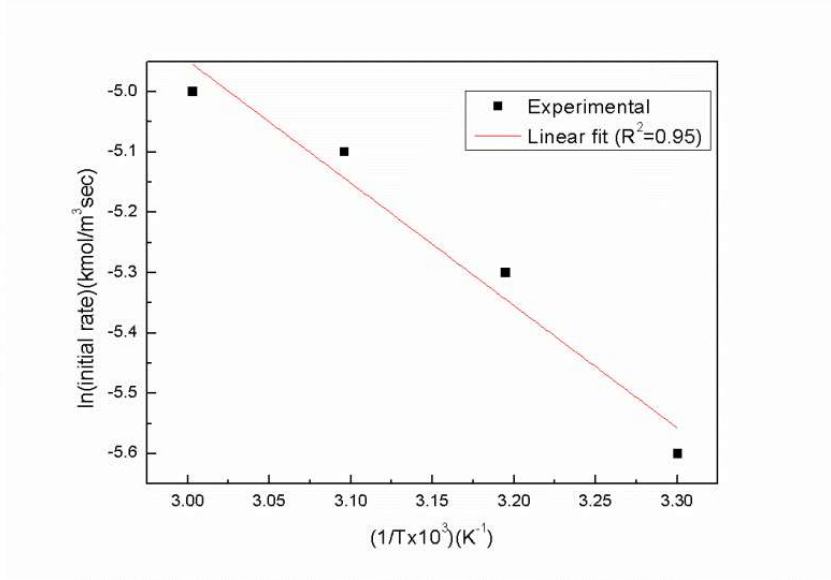
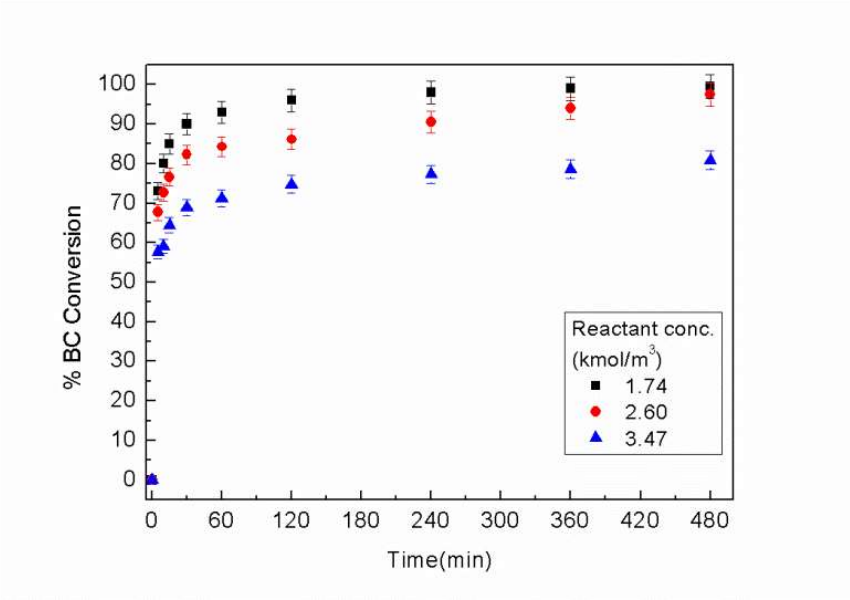
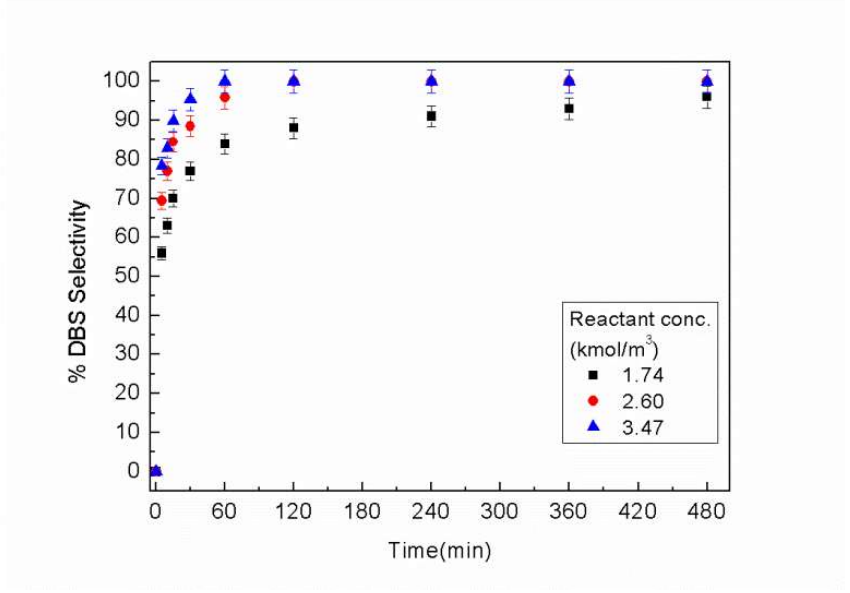


Figure 5.4: Arrhenius plot of ln(initial reaction rate) vs. 1/T. All other conditions are same as Fig. 4.

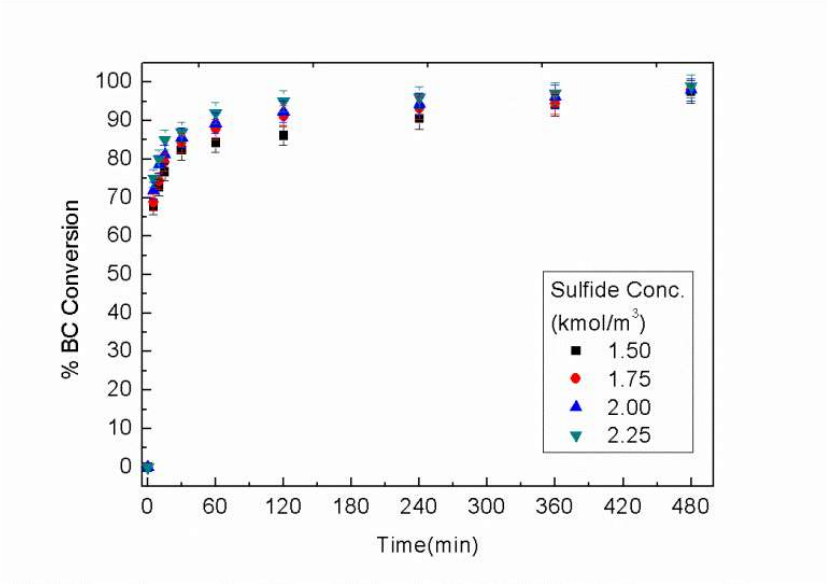


(a)

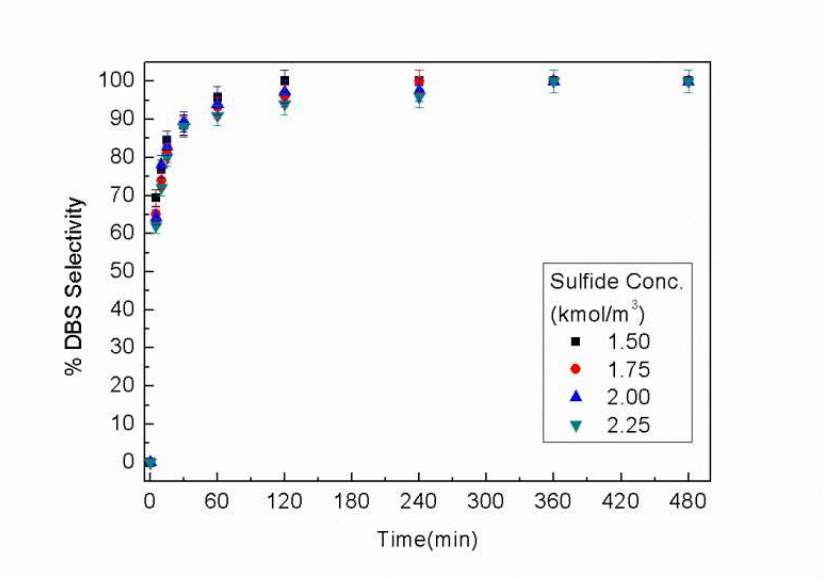


(b)

Figure 5.5: Effect of BC concentration on (a) BC conversion (b) DBS selectivity. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5} m^3 each; concentration of catalyst = 0.03 kmol/m^3 org. phase; concentration of toluene = 6.6 kmol/m^3 in org. phase; phase; MDEA conc. = 3.05 kmol/m^3; concentration of sulfide = 1.5 kmol/m^3; temperature = 323 K.

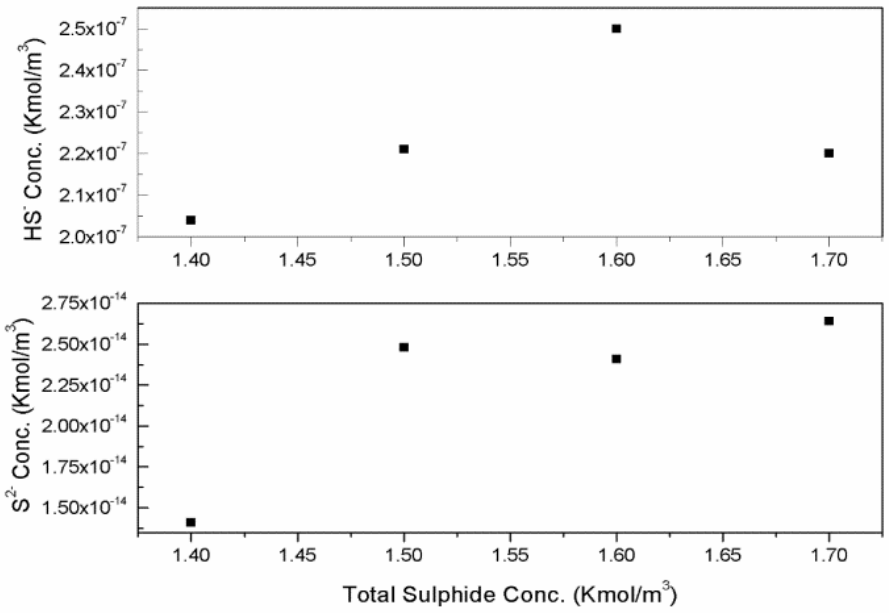


(a)

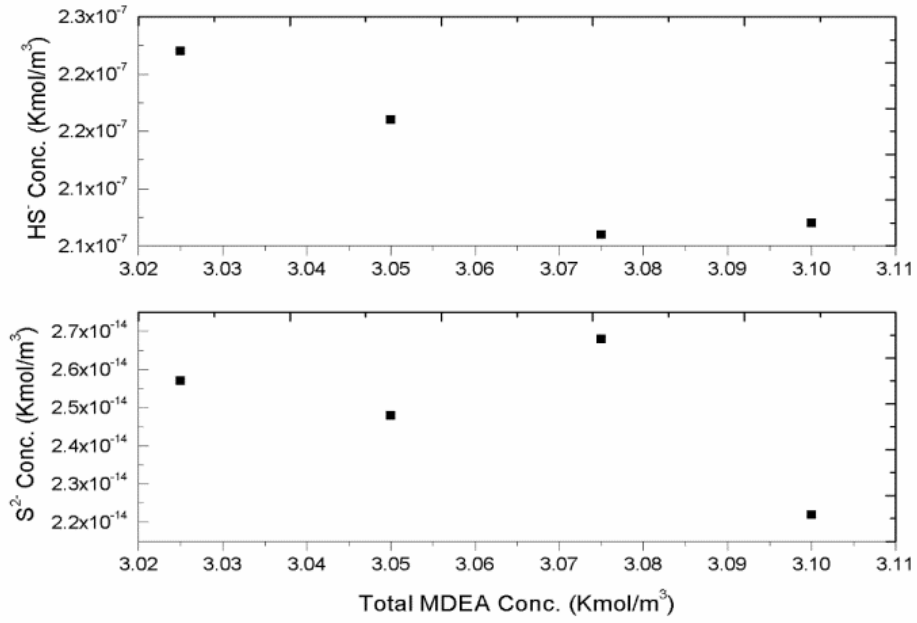


(b)

Figure 5.6: Effect of sulfide concentration on (a) BC conversion (b) DBS selectivity. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5} m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; MDEA conc. = 3.05 kmol/m^3; concentration of catalyst = 0.03 kmol/m^3 org. phase; temperature = 323 K.

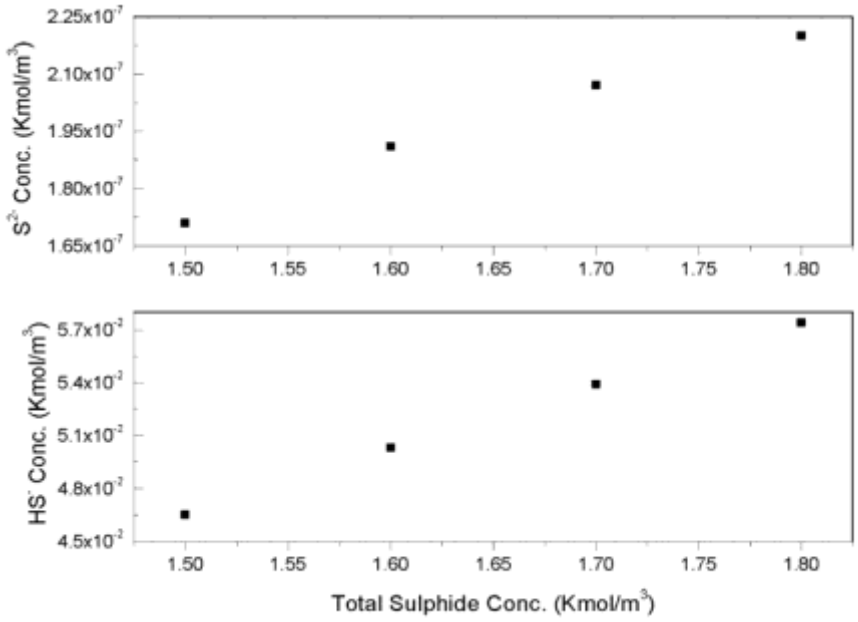


(a)

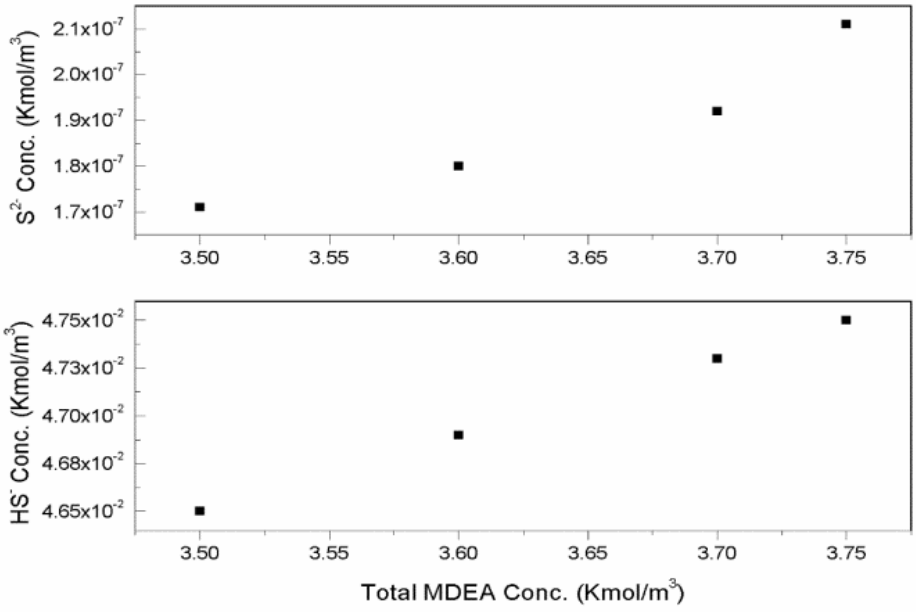


(b)

Figure 5.7: Effect of (a) low sulfide and (b) low MDEA concentration on the formation of hydrosulfide and sulfide ions.



(a)



(b)

Figure 5.8: Effect of (a) low sulfide and (b) high MDEA concentration on the formation of hydrosulfide and sulfide ions.

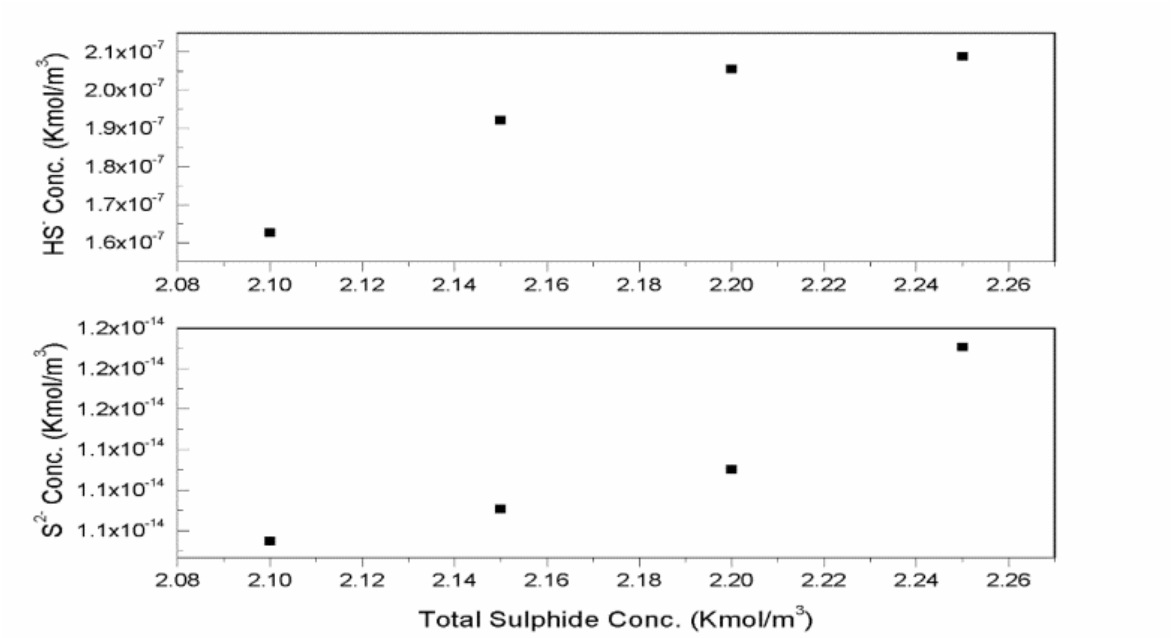


Figure 5.9: Effect of high sulfide concentration on the formation of hydrosulfide and sulfide ions.

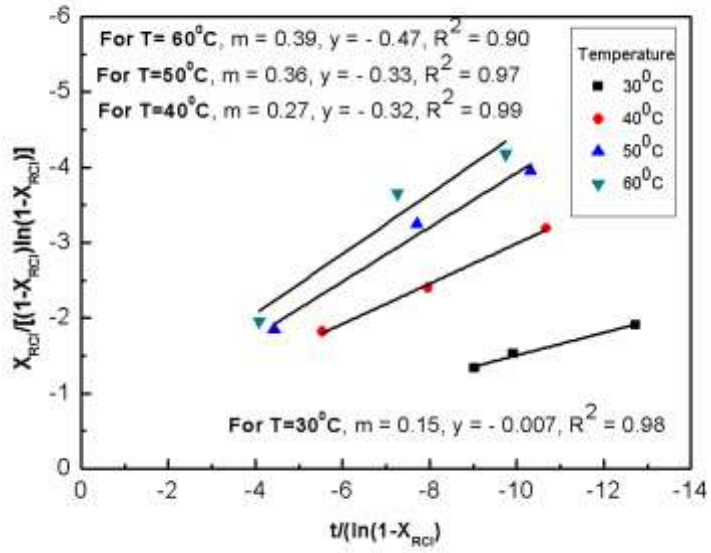


Figure 5.10: Validation of the kinetic model with experimental data at different temperature. Operating conditions: volume of organic phase = $5.0 \times 10^{-5} m^3$, volume of aqueous phase = $5.0 \times 10^{-5} m^3$, concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of BC = 2.6 kmol/m^3in org. phase, concentration of catalyst = 0.03 kmol/m^3 org. phase; sulfide concentration = 1.5 kmol/m^3; stirring speed = 1500 rpm.

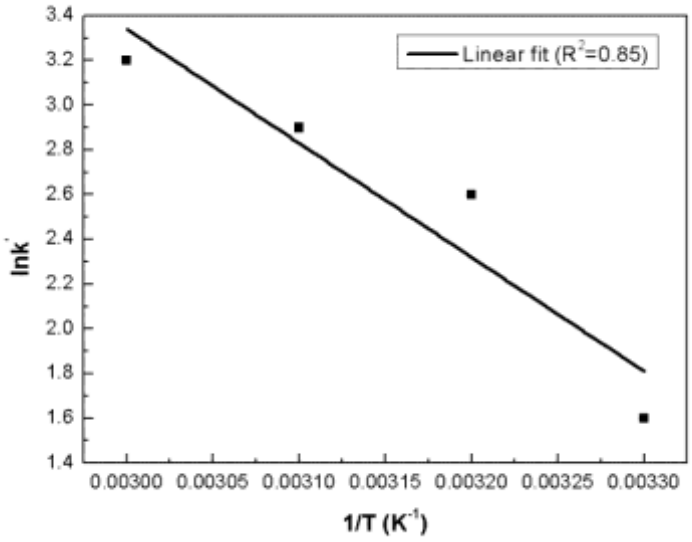


Figure 5.11: Arrhenius plot of ln (k') vs 1/T. All other conditions are same as Fig. 5.12.

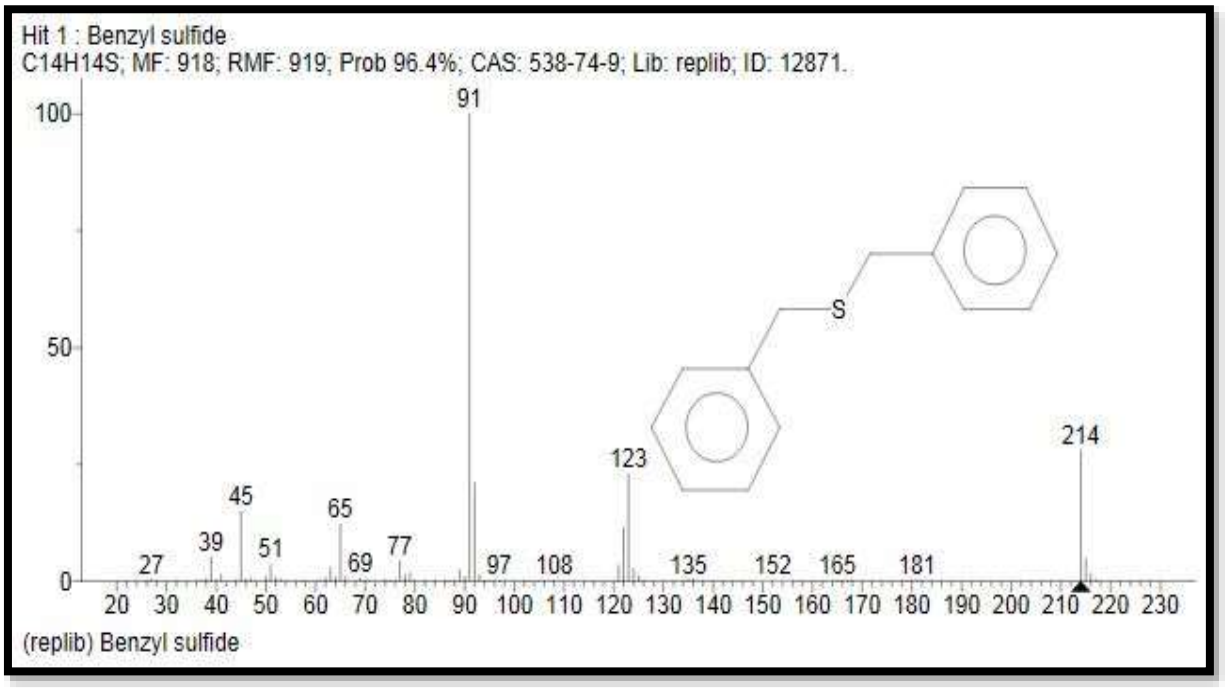


Figure 5.12: MS spectra for DBS

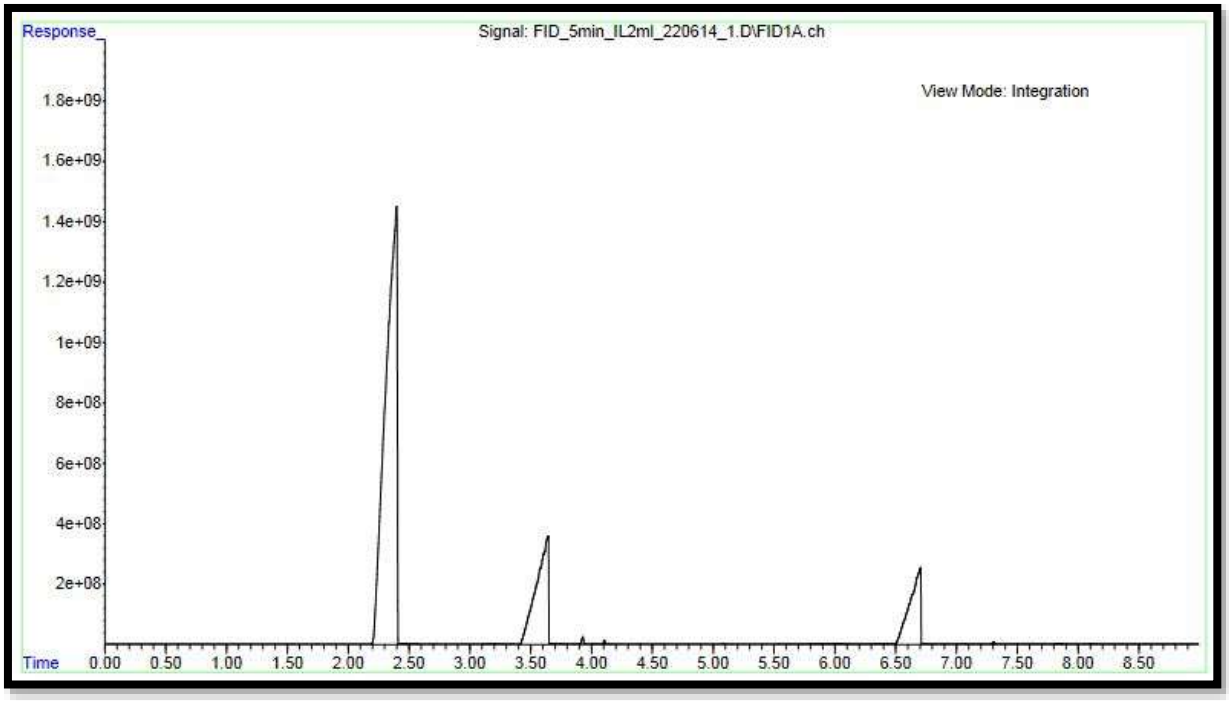


Figure 5.13: GLC chromatogram for DBS after 5 min of reaction time in presence of THTDPC

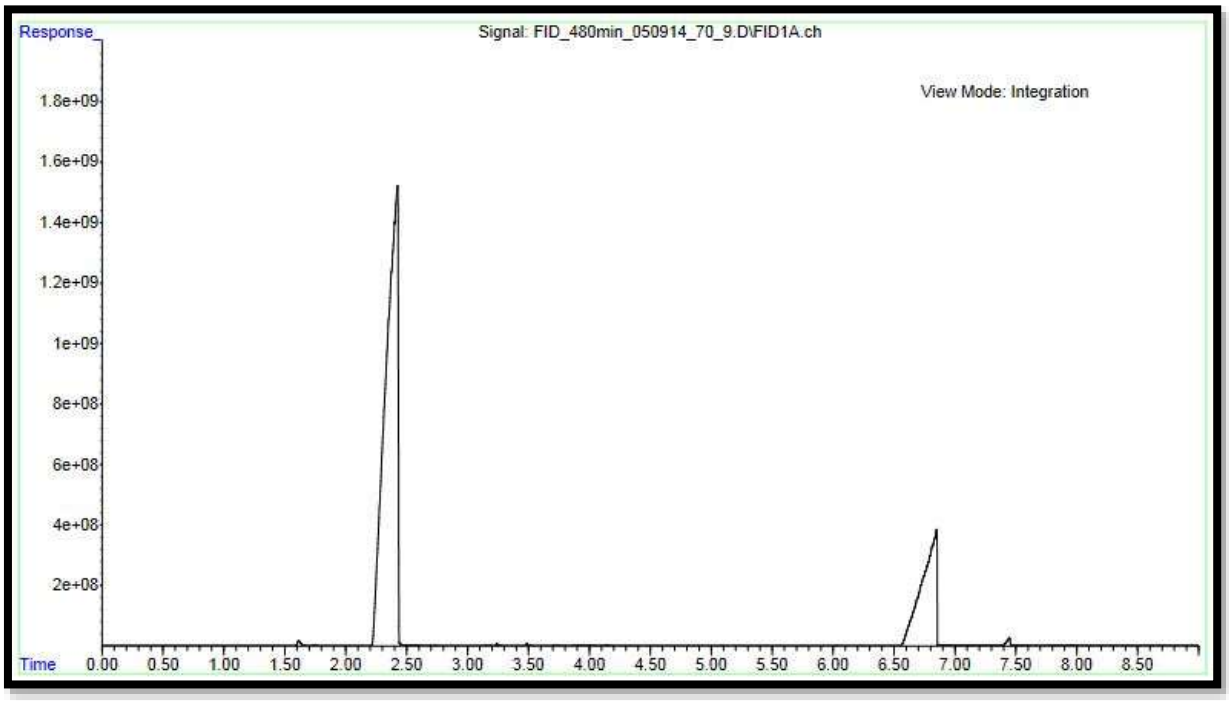


Figure 5.14: GLC chromatogram for DBS after 480 min of reaction time in presence of THTDPC

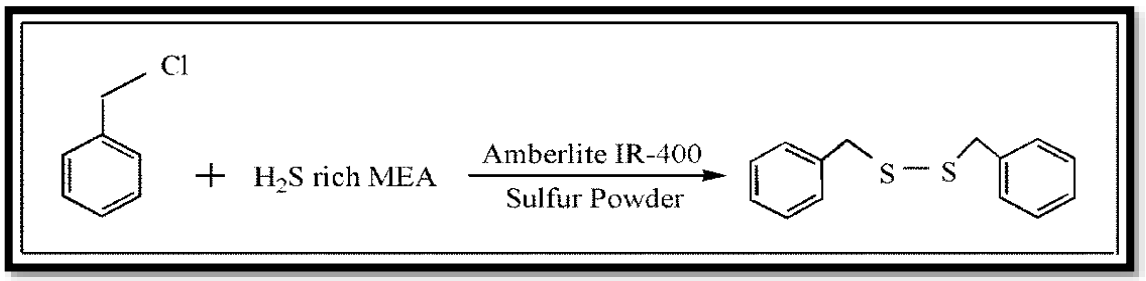
Chapter 6

Synthesis of Dibenzyl Disulfide with H_2S-Laden Monoethanolamine under Liquid–Liquid–Solid Phase Transfer Catalysis

This chapter deals with the detailed kinetic investigation for the selective synthesis of dibenzyl disulfide (DBDS) from the reaction of benzyl chloride (BC) and H_2S-rich aqueous monoethanolamine (MEA) and elemental sulfur under liquid-liquid-solid phase transfer catalysis (L-L-S PTC). The investigation includes the effect of different parametric on BC conversion and DBDS selectivity, mechanistic investigation and kinetic modeling. Effect of temperature, catalyst loading, BC/sulfide mole ratio, initial sulfide concentration and MEA concentration on BC conversion and DBDS selectivity were investigated under parametric study.

6.1 Introduction

In the present study, the synthesis of dibenzyl disulfide (DBDS) was done by the reaction of benzyl chloride with aqueous H_2S-rich MEA and elemental sulfur under liquid-liquid-solid (L-L-S) phase transfer catalysis. DBDS was the only product detected after the completion of the reaction by gas-liquid chromatography. The applications and importance of DBDS have already been discussed in Chapter 2. Moreover, there is a possibility of benzyl alcohol and N-benzyl MEA by alkaline hydrolysis and chlorine atom substitution respectively, but none of them was detected in GLC analysis after the course of the reaction. The overall reaction can be represented by Scheme 6.1.



Scheme 6.1: Overall Reaction

A Parametric studies have been performed to observe the effect of different parameters such as agitation speed, temperature, catalyst concentration, BC concentration, sulfide concentration and MEA concentration on BC conversion and DBDS selectivity, a

suitable mechanism was proposed to explain the course of the reaction and a kinetic model has been developed.

6.2 Result and discussion

6.2.1 Parametric study

6.2.1.1 Effect of stirring speed

The speed of agitation was varied from 1000 to 2500 rpm in both the conditions, with and without catalyst to determine the effect of mass transfer resistance of reactants on the reaction rate. Fig. 6.1 shows that rate of reaction is practically same in all stirring speeds. Therefore, it can be assumed that beyond 1500 rpm, an increase in stirring speed has no influence on reaction rate. So, the reaction can be safely considered as a kinetically controlled reaction. Thus, the further synthesis was carried out at 1500 rpm to remove mass transfer resistance. In the absence of a catalyst, the rate of reaction is very low. Therefore, further experiments have been performed in the presence of catalyst only.

6.2.1.2 Effect of sulfur loading

Addition of sulfur powder in H_2S-rich MEA leads to the formation of disulfide and polysulfide anions S_x^{2-} (where x = 2, 3, 4) (Sonavane, Chidambaram, Almog, & Sasson, 2007). Different concentrations of elemental sulfur was weighed and dissolved in H_2S-rich MEA and the colour of aqueous solution was found to change to reddish brown from greenish.

Sulfide (S^{2-}) and hydrosulfide (HS^-) were found to be the dominating species at low sulfur loading and gives DBS and BM respectively as the product (Sen, Maity, Pradhan, & Patwardhan, 2007). In the absence of elemental sulfur, there was no formation of DBDS and at 0.25 and 0.49 of sulfur to sulfide mole ratio, selectivity of DBDS was found to be very low (Fig. 6.2). At 0.99 and 1.24 sulfur to sulfide mole ratio, formation of polysulfide anions $S_{3,4,5}^{2-}$ is more and gives undesired side products. DBDS selectivity was observed 100% at 0.74 sulfur to sulfide mole ratio as it ensures only the formation of disulfide (S_2^{2-}) anions. So 1.875 kmol/m^3 of sulfur was considered as an optimum reaction parameter and further experiments were performed at this condition.

6.2.1.3 Effect of catalyst concentration

The effect of catalyst concentration on the conversion of BC was noticed in both the conditions, in the absence and presence of PTC (Fig. 6.3). The concentration of catalyst was varied from zero to 0.58 kmol/m^3 and it was observed that when the catalyst was absent, the maximum BC conversion was 61% even after 480 min of reaction run. It was noticed that BC conversion drastically increased with increase in catalyst concentration.

Disulfide (S_2^{2-}) anions present in the aqueous phase reacts with cation (Q^+) of PTC and makes a catalyst active intermediates Q_2S_2. The active ion pair Q_2S_2 crosses the interface and reaches into the organic phase where it reacts with an organic reactant BC to yield the desired product DBDS.

Table 6.1 shows initial reaction rate enhancement with different catalyst concentrations as compare to the reaction rate in the absence of PTC. Enhancement factor indicates the significance of amberlite IR-400 as a PTC in the synthesis of DBDS.

Table 6.1: Effect of catalyst loading on Initial reaction rate

Concentration of Amberlite IR-400 (kmol/m^3 org phase)	**Initial reaction rate (kmol/m^3s) at 5% Conversion**	**Enhancement factor**
0.00	2.22×10^{-3}	1.0
0.15	3.50×10^{-3}	1.6
0.29	4.85×10^{-3}	2.2
0.44	6.7×10^{-3}	2.8
0.58	7.55×10^{-3}	3.4

All other conditions are same as Fig. 6.3.

In order to obtain the order of reaction with respect to PTC, the natural logarithm of initial reaction rate was calculated for all PTC concentration and was plotted against the natural logarithm of PTC concentration (Fig. 6.4). The order of reaction was obtained as 0.55 with respect to the catalyst concentration from the graph which can be considered as first order w.r.t. the catalyst concentration.

6.2.1.4 Effect of temperature

BC conversion studied in this section at four different temperatures ranges between 303 to 333K, and other parameters were kept constants. Fig 6.5 shows the effect of temperature on the conversion of BC, and it is found that with an increase in temperature BC conversion also increases.

The initial reaction rate of every experimental run performed at different temperatures was calculated, and Arrhenius plot was obtained by plotting a graph between ln of initial reaction rate and 1/T (K^{-1}). The activation energy was obtained from the graph as 56.03 kJ/mol.

6.2.1.5 Effect of benzyl chloride concentration

The influence of varying initial BC/Sulfide mole ratio on BC conversion was investigated by keeping other parameter constant. It was observed that with an increase in the initial BC/sulfide mole ratio, BC conversion decreases (Fig. 6.7) due to the presence of limited disulfide anions in the aqueous phase. At 1.04 BC/sulfide mole ratio, optimum BC conversion was observed and it was reduced to 94% in case of 1.39 BC/sulfide mole ratio. So further experiments were performed at 1.04 BC/sulfide mole ratio to ensure the optimum conversion.

From the plot of ln(initial rate) vs. ln(concentration of BC) (Fig. 6.8), the order of reaction with respect to BC concentration was obtained as 2.44, which is close to 2. Hence, the order of reaction is second order with respect to the concentration of reactant.

6.2.1.6 Effect of sulfide concentration

The effect of sulfide concentration on BC conversion was observed by varying it from 1.75 to 2.5 kmol/m^3 keeping MEA concentration constant (35 wt %). At 2.50 kmol/m^3 sulfide concentration, 98%, BC conversion was obtained. It decreased gradually with a decrease in sulfide concentration (Fig. 6.9).

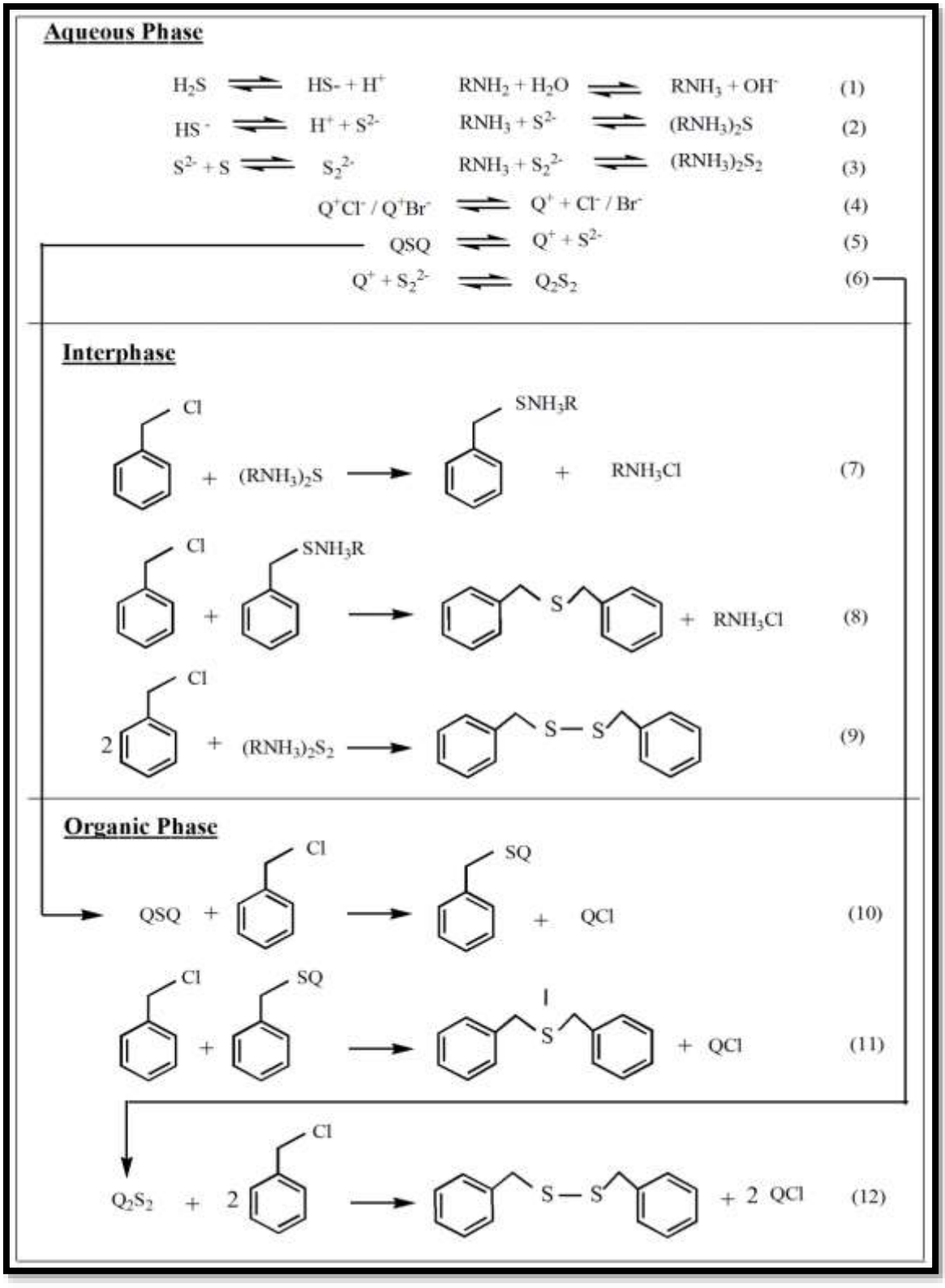
From the plot of ln (initial rate) against ln(initial sulfide concentration) (Fig. 6.10), the slope of the linear fit line was found out to be to be 2.14. Since this value is closer to 2, the reaction was considered second order with respect to the sulfide concentration.

6.2.1.7 Catalyst Recovery and Reuse

Agitation of the reaction mixture was stopped after 480 min of experimental run and the reaction mixture transferred into the separating funnel. Sufficient time was given for the phase settlement, and organic phase remained at the top while aqueous phase at the bottom. The organic phase was removed from the top, and the PTC remained in the aqueous phase was recovered using filter paper. Initially, acetone was used to wash the recovered catalyst then it was washed with the solution of NaCl and dried at 50 ^{0}C in an oven. The catalyst was recovered, regenerated and reused for four times and the results are shown in Fig.6.11. We can say that up to four times the performance of catalyst was excellent, but the BC conversion was decreased due to loss of catalyst during separation and washing.

6.3 Proposed mechanism of synthesis of dibenzyl disulfide under L-L-S PTC

The reaction mechanism for synthesizing DBDS from the reaction of BC and H_2S-rich MEA with added elemental sulfur is represented in Scheme 6.2.The reactions in the aqueous phase are generally faster than the organic phase reactions. So, there is an existence of an ionic equilibrium between RNH_2 (MEA), H_2O and H_2S that leads to the formation of three nucleophiles in the aqueous phase, named as, disulfide (S_2^{2-}), sulfide (S^{2-}) and hydroxide. In the present work, due to the presence of elemental sulfur, HS^- ions is not expected to stay in the aqueous phase. The presence of elemental sulfur shifts the ionic equilibrium and only S_2^{2-} and S^{2-}ions forms. The synthesis of DBDS was achieved from both, non-catalytic and catalytic pathways.



Scheme 6.2. Proposed mechanism of synthesis of DBDS by H_2S-laden MEA under L-L-S PTC

6.3.1 Non- catalytic Contribution

In Scheme 6.2, reaction (2) and (3) shows the formation of ethanolamine disulfide ($(RNH_3)_2S_2$) and ethanolamine sulfide ($(RNH_3)_2S$). These intermediates are not lipophilic, so they stay in the aqueous phase only and reacts with BC at the interphase. The reaction of these intermediates with BC yield DBS and DBDS according to the reaction (7)-(9).

6.3.2 Catalytic contribution

In the presence of solid catalyst, surface reaction and mass transfer are two important factors to explain the course of the reaction (Satrio, Glatzer, & Doraiswamy, 2000). At first, S_2^{2-} and S^{2-}anions diffuse into the PTC from the bulk phase and ion exchange reaction takes place between cation (Q^+) and nucleophiles. This step leads to the formation of active intermediates Q_2S_2 and QSQ represented by reaction (4)-(6). These intermediates travel to the organic phase by crossing the interphase where BC reacts with Q_2S_2 and QSQ, and formation of DBS and DBDS takes place according to reaction (10)-(12) in Scheme 6.2.

6.4 Kinetic modeling

The GC analysis shows that the formation of DBS is very less as compared to DBDS. This observation can be attributed to less diffusion of aqueous sulfide (S^{2-}) anion in comparison to disulfide (S_2^{2-}) anion in the aqueous phase and the corresponding insignificant formation of catalyst active intermediate QSQ as compare to Q_2S_2 in the ion exchange step. The overall rate of reaction between the organic substrate RCl and a di-ionic inorganic nucleophile S_2^{2-} to form organic product RS_2R in the presence of PTC, Q^+Cl^- then can be expressed as a function of the concentrations of RCl and $Q^+S_2^{2-}Q^+$, i.e.

$$2\ RCl + Q^+S_2^{2-}Q^+ \rightarrow RS_2R + 2\ Q^+Cl^- \tag{13}$$

$$\text{Rate}, -r_{org} = -\frac{d[RCl]_{org}}{dt} = k_{org}[RCl]^2_{org}[Q^+S_2^{2-}Q^+]_s \tag{14}$$

In the present work, a rigorous model based on the modification of the Langmuir-Hinshelwood/Eley-Rideal mechanism has been developed, and experimental data from the reaction between benzyl chloride in the organic phase and disulfide in the aqueous phase to yield dibenzyl disulfide has been used to verify it. This reaction system belongs to a general class of esterification reactions where the nucleophile is extracted from the aqueous phase using a phase transfer catalyst. The reaction is mediated by polymer-supported quaternary ammonium chloride and conducted in the batch slurry mode.

The whole reaction can be compared to the Eley-Rideal reaction mechanism (Satrio et al., 2000), which includes the reaction between an adsorbed reactant with an un-adsorbed reactant from the bulk phase. Here, ion-exchange step can be considered as the adsorption of the first reactant to convert inactive sites into active sites, and in organic phase reaction step, the second reactant reacts with adsorbed reactant to yield desired product RS_2R.

We assume that the reaction mechanism consists of an ion-exchange reaction step between S_2^{2-} and Q^+X^- to form an active site, $Q^+S_2^{2-}Q^+$ followed by reaction of RCl at this site to form a final product, RS_2R, and an inactive site, Q^+Cl^-. These steps may be described as follows:

Ion Exchange step:

$$2\,(Q^+Cl^-)_s + (S_2^{2-})_{aq} \leftrightarrow (Q^+S_2^{2-}Q^+)_s + 2\,(Cl^-)_{aq} \tag{15}$$

Organic phase reaction step:

$$(Q^+S_2^{2-}Q^+)_s + 2\,(RCl)_{org} \leftrightarrow 2\,(Q^+Cl^-)_s + (RS_2R)_{org} \tag{16}$$

The reversible ion-exchange step may be compared to the Langmuir-Hinshelwood adsorption/desorption mechanism. We can express the Eq. (15) using traditional notations of heterogeneous catalysis as,

$$(S_2^{2-}) + 2\,(Q^+Cl^-) \leftrightarrow 2\,(Cl^-) + (Q^+S_2^{2-}Q^+) \tag{17}$$

Where Q^+ is catalyst's cation.

Assuming the formation of transitional site $Cl^-Q^+S_2^{2-}Q^+Cl^-$ between the forward and backward reaction steps, the whole reaction can be written as,

$$(S_2^{2-}) + 2\,(Q^+Cl^-) \leftrightarrow Cl^-Q^+S_2^{2-}Q^+Cl^- \leftrightarrow 2\,(Cl^-) + (Q^+S_2^{2-}Q^+) \quad (18)$$

We can split the ion exchange step as two separate equilibrium attachment/detachment steps. The attachment/detachment of S_2^{2-} anion on the inactive site of Q^+Cl^- can be seen in the forward reaction step as,

$$2\,(Q^+Cl^-)_s + (S_2^{2-})_{aq} \leftrightarrow Cl^-Q^+S_2^{2-}Q^+Cl^- \quad (19)$$

Similarly, attachment/detachment of Cl^- anion on an active site of $Q^+S_2^{2-}Q^+$ can be seen in the backward reaction step as,

$$(Q^+S_2^{2-}Q^+)_s + 2\,(Cl^-)_{aq} \leftrightarrow Cl^-Q^+S_2^{2-}Q^+Cl^- \quad (20)$$

Assuming the rates of attachment/detachment are in equilibrium, Eq. (21) and Eq. (22) can be obtained from Eq. (19) and (20), respectively as,

$$\theta_{ClS} = K_S[S_2^{2-}]_{aq}(1 - \theta_S - \theta_{ClS}) \quad (21)$$

$$\theta_{ClS} = K_{Cl}[Cl^-]_{aq}^2(1 - \theta_{Cl} - \theta_{ClS}) \quad (22)$$

Where, K_S and K_{Cl} are the equilibrium attachment/detachment constants for S_2^{2-} and Cl^- anions, respectively; $[S_2^{2-}]$ and $[Cl^-]$ are the concentrations of S_2^{2-} and Cl^- anions in the aqueous phase, respectively; and θ_S, θ_{Cl}, θ_{ClS} are the fractions of the total number of triphase catalyst cations attached to S_2^{2-}, Cl^- and both S_2^{2-} and Cl^-anions, respectively.

Mathematically, this can be written as: $\theta_{Cl} + \theta_{ClS} + \theta_S = 1$, which signifies that the total of all the fractions of active and inactive sites of the catalyst equals to unity. It is assumed that once, transition sites $Cl^-Q^+S_2^{2-}Q^+Cl^-$ are formed, they are instantaneously transformed either into active sites $Q^+S_2^{2-}Q^+$ or inactive sites Q^+Cl^-. At any instant of time there is very less fraction of transition site (θ_{ClS}) present in the reaction mixture as compare to active and inactive sites (θ_{Cl} and θ_S) but can't be neglected. So, $\theta_{Cl} + \theta_S \approx 1$. Eq. (21) and (22) can be re-written as

$$\theta_S = K_S[S_2^{2-}]_{aq}(1 - \theta_S - \theta_{Cl}) \quad (23)$$

$$\theta_{Cl} = K_{Cl}[Cl^-]^2_{aq}(1 - \theta_S - \theta_{Cl}) \quad (24)$$

We have obtained a hyperbolic equation for the fraction of active PTC sites by combining the expressions for θ_S and θ_{Cl} as

$$\theta_S = \frac{K_S[S_2^{2-}]_{aq}}{1+K_{Cl}[Cl^-]^2_{aq}+K_S[S_2^{2-}]_{aq}} \quad (25)$$

We can also write above equation in terms of catalyst concentration,

$$[Q^+S_2^{2-}Q^+] = [Q^+]_{tot}\frac{K_S[S_2^{2-}]_{aq}}{1+K_{Cl}[Cl^-]^2_{aq}+K_S[S_2^{2-}]_{aq}} \quad (26)$$

Where, $[Q^+]_{tot}$ and $[Q^+S_2^{2-}Q^+]$ are the total concentrations of catalyst and the concentration of catalyst attached to S_2^{2-} anions, respectively.

We obtain Eq. (27) for the rate of the organic reactions by combining Eq. (14) and Eq. (26) as,

$$-r_{org} = -\frac{d[RCl]_{org}}{dt} = k_{org}[RCl]^2_{org}[Q^+]_{tot}\frac{K_S[S_2^{2-}]_{aq}}{1+K_{Cl}[Cl^-]^2_{aq}+K_S[S_2^{2-}]_{aq}} \quad (27)$$

$$-\frac{d[RCl]_{org}}{dt} = k_{org}[RCl]^2_{org}[Q^+]_{tot}\frac{K_S[S_2^{2-}]_{aq}}{1+K_{Cl}[Cl^-]^2_{aq}+K_S[S_2^{2-}]_{aq}} \quad (28)$$

Let us introduce fractional conversion of reactant (X_{RCl}), which can be calculated as

$$X_{RCl} = \frac{[RCl]_{org,0}-[RCl]_{org}}{[RCl]_{org,0}} \quad (29)$$

Where, $[RCl]_{org,0}$ and $[RCl]_{org}$ represents initial concentration of benzyl chloride and BC concentration at any time respectively. Now we can write Eq. (28) in the form of fractional conversion as

$$-r_{org} = \frac{dX_{RCl}}{dt} = k_{org}[RCl]_{org,0}[Q^+]_{tot}\frac{K_S[S_2^{2-}]_{aq}(1-X_{RCl})^2}{1+K_{Cl}[Cl^-]^2_{aq}+K_S[S_2^{2-}]_{aq}} \quad (30)$$

$$= \frac{dX_{RCl}}{(1-X_{RCl})^2} = k_{org}[RCl]_{org,0}[Q^+]_{tot}\frac{K_S[S_2^{2-}]_{aq}}{1+K_{Cl}[Cl^-]^2_{aq}+K_S[S_2^{2-}]_{aq}}dt \quad (31)$$

$$= \frac{dX_{RCl}}{(1-X_{RCl})^2} = k_{app}dt \quad (32)$$

Where $k_{app} = k_{org}[RCl]_{org,0}[Q^+]_{tot}\frac{K_S[S_2^{2-}]_{aq}}{1+K_{Cl}[Cl^-]_{aq}^2+K_S[S_2^{2-}]_{aq}}$. The terms in the k_{app} can be calculated experimentally. Thus, after integration of Eq. (32) we get,

$$\frac{X_{RCL}}{1-X_{RCL}} = k_{app}t \quad (33)$$

From the Eq. (33) it is clear that the reaction follows second order kinetics.

6.5 Validation of kinetic model

The kinetic model was validated by considering Eq. (33) was valid at different temperatures by plotting of $X_{RCl}/(1-X_{RCl})$ against time (Fig. 6.12). The slope of each line gives apparent rate constant k_{app} at different temperatures as shown in Table 6.2. Fig. 6.13 shows a comparison of calculated conversions of BC based on apparent rate constants and experimentally obtained conversions of BC. Good agreement has been observed between calculated and experimental conversions.

Table 6.2. Apparent rate constants (k_{app}) at different temperatures

Temperature (°C)	30	40	50	60
$\boldsymbol{k_{app}}$**(min^{-1})**	0.01673	0.03276	0.05033	0.10171

All the considerations are same as mentioned in Fig. 6.12.

6.6 Identification and quantification

The product was identified using GC-MS (Agilent 5977A). The temperature programming followed is mentioned in Chapter 3. DBDS compound was successfully identified from the analysis and the graph obtained from GC-MS is represented in Fig. 6.14.

The quantification of the product was done using GC-FID (Agilent GC 7890B). The temperature programming followed is mentioned in Chapter 3. Each sample was

analyzed using GC-FID, and the kinetic study was performed. As an example, initial and final graphs of one parameter are represented in Fig. 6.15 and 6.16.

6.7 Conclusion

A detailed study has been carried out on the synthesis of DBDS from BC using amberlite IR-400 as a solid phase transfer catalyst. It is seen that at a different speed of agitation there was no significant change in the rate of reaction and so the reaction was found to be kinetically controlled and all experiments were done at a speed of 1500 rpm. The reaction was found to be approximately first order with respect the concentration of the catalyst, second order with respect to the reactant concentration and second order with respect to the sulfide concentration. 100% selectivity of DBDS was observed at 1.875 kmol/m^3 of sulfur loading. The obtained activation energy, for DBDS synthesis, from Arrhenius plot was 56.03 kJ/mol. The catalyst was recovered and reused four times with successive decrease in the conversion of BC. A mathematical model was developed, based on kinetic study and proposed mechanism, to account for the calculation of the rate constant and it was validated using experimental data.

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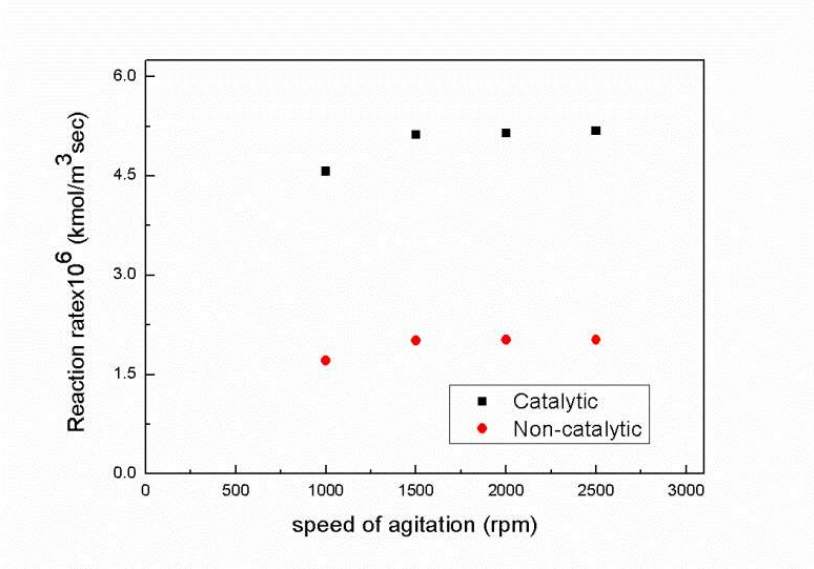


Figure: 6.1: Effect of stirring speed on the rate of reaction. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5} m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of catalyst = 0.29 kmol/m^3 in org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; MEA/H_2S mole ratio = 2.28; concentration of sulfide = 2.53 kmol/m^3; Sulfur loading= 1.875 kmol/m^3; temperature = 323 K.

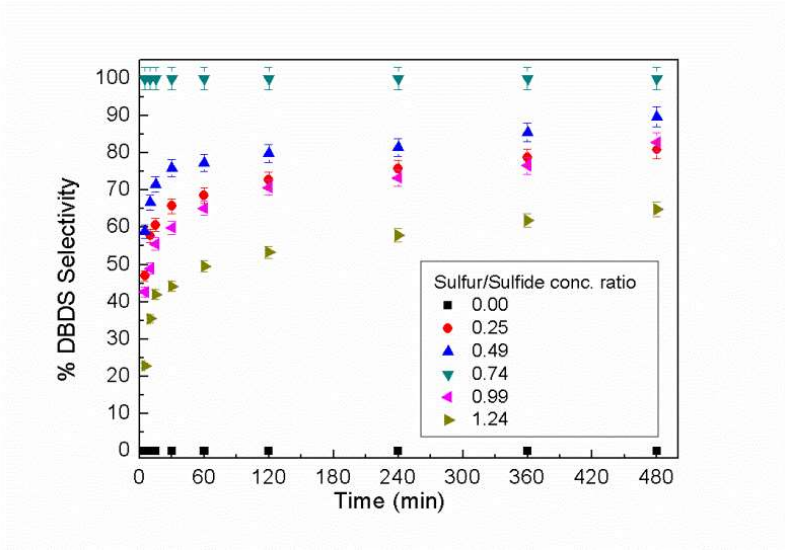


Figure 6.2: Effect of elemental sulfur loading on DBDS selectivity. Operating conditions: volume of aqueous and organic phase = $5.0\times\ 10^{-5}$m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of BC= 2.6 kmol/m^3 in org. phase; concentration of catalyst = 0.29 kmol/m^3 in org phase; MEA/H_2S mole ratio = 2.28; concentration of Sulfide = 2.53 kmol/m^3; agitation speed= 1500 rpm; temperature = 323 K.

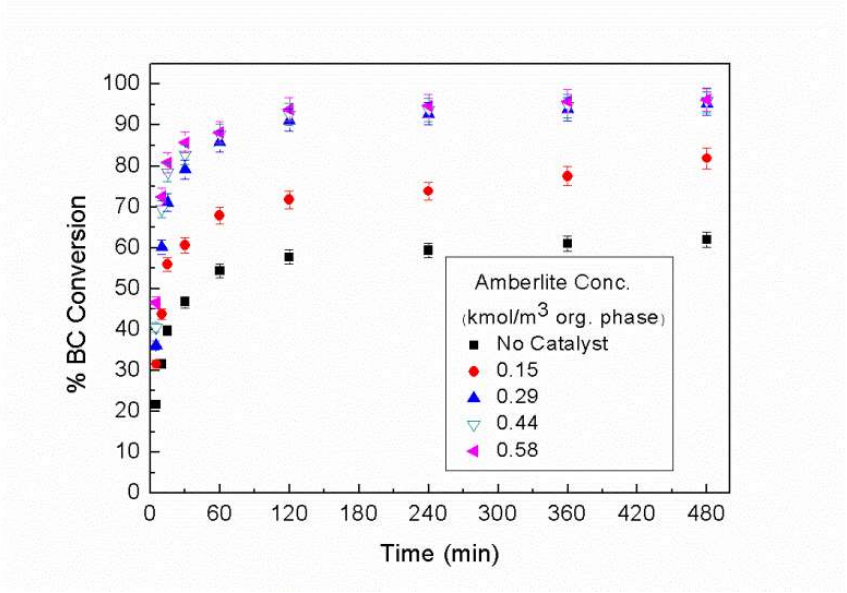


Figure 6.3: Effect of catalyst loading on BC conversion. Operating conditions: volume of aqueous and organic phase = $5.0\times\ 10^{-5}$m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of BC = 2.6 kmol/m^3 in org. phase; MEA/H_2S mole ratio = 2.28; concentration of sulfide = 2.53 kmol/m^3; temperature = 323 K; agitation speed= 1500 rpm; sulfur loading= 1.875 kmol/m^3.

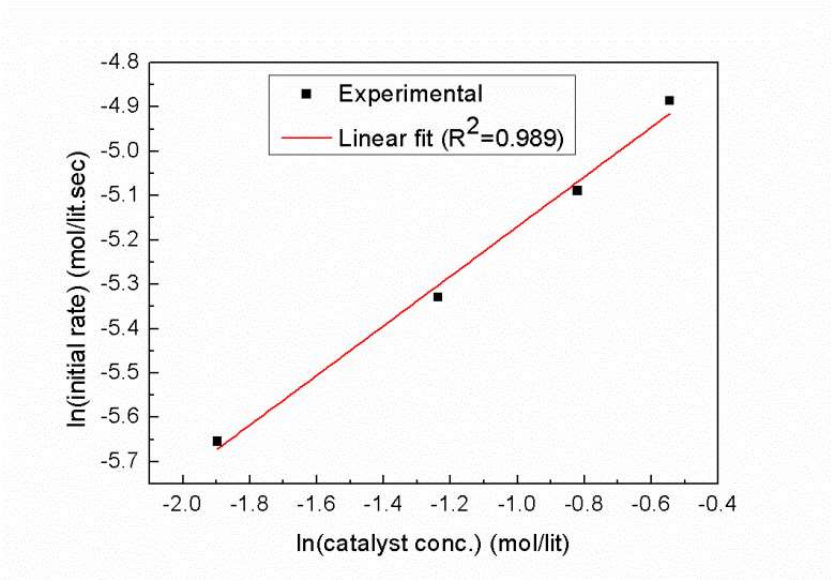


Figure 6.4: Plot of ln (initial reaction rate) vs ln (catalyst concentration). All other conditions are same as Fig. 6.3.

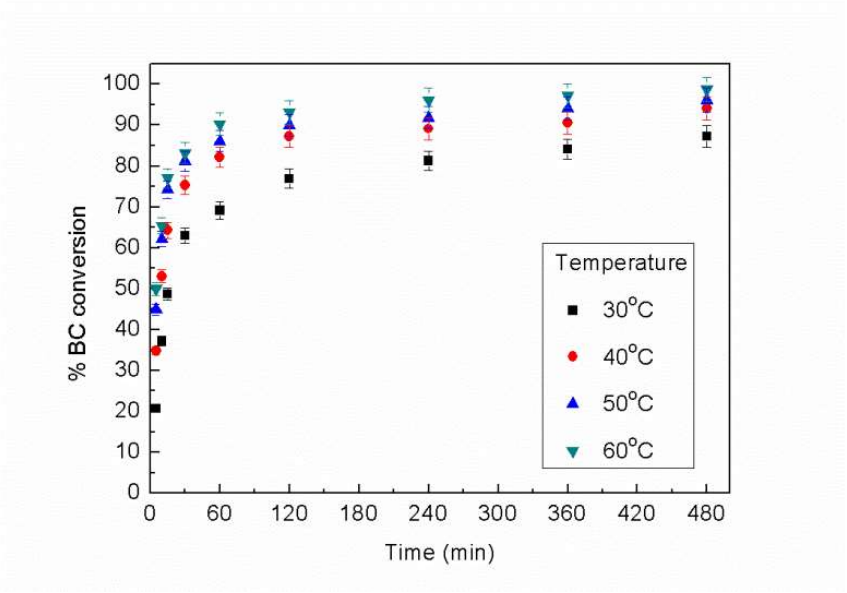


Figure 6.5: Effect of temperature on BC conversion. Operating conditions: volume of aqueous and organic phase = $5.0\times\ 10^{-5}$m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of catalyst = 0.29 kmol/m^3 in org phase; concentration of BC = 2.6 kmol/m^3 in org. phase; MEA/H_2S mole ratio = 2.28; concentration of sulfide = 2.53 kmol/m^3; agitation speed= 1500 rpm; sulfur loading= 1.875 kmol/m^3.

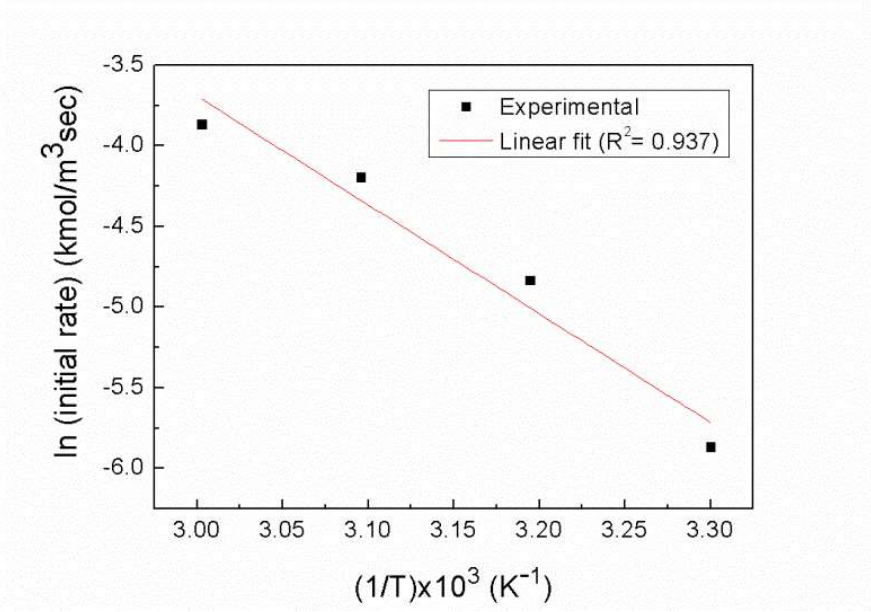


Figure 6.6: Arrhenius plot of ln (initial reaction rate) vs 1/T. All other conditions are same as Fig. 6.5.

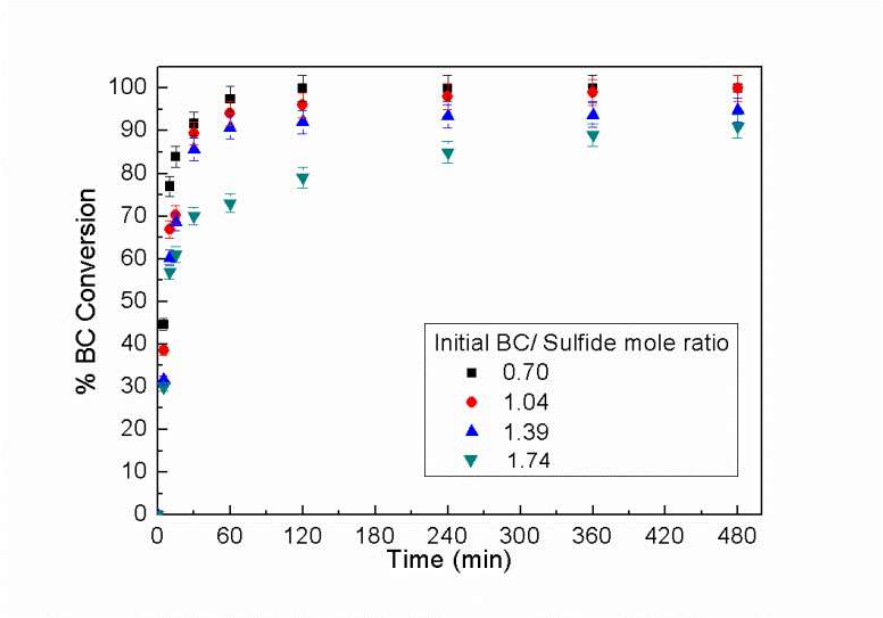


Figure 6.7: Effect of BC concentration on reactant conversion. Operating conditions: volume of aqueous and organic phase = $5.0\times\ 10^{-5}$m^3 each; concentration of catalyst = 0.29 kmol/m^3 in org phase; MEA/H_2S mole ratio = 2.28; concentration of sulfide = 2.53 kmol/m^3; agitation speed= 1500 rpm; sulfur loading= 1.875 kmol/m^3.

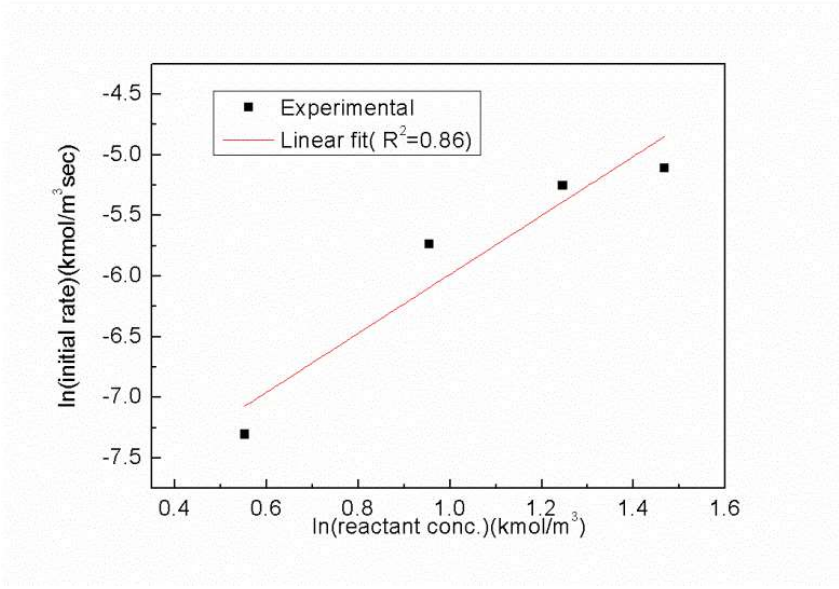


Figure 6.8: Plot of ln(initial rate) vs. ln(reactant concentration). All other conditions are same as Fig. 6.7.

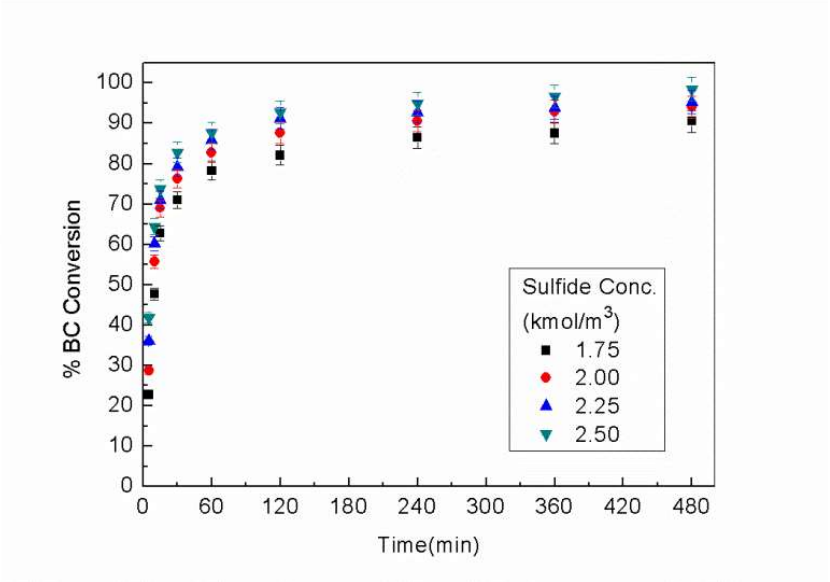


Figure 6.9: Effect of sulfide concentration on BC conversion. Operating conditions: volume of aqueous and organic phase = 5.0×10^{-5}m^3 each; concentration of toluene = 6.6 kmol/m^3 in org. phase; concentration of catalyst = 0.29 kmol/m^3 in org phase; concentration of BC = 2.6 kmol/m^3 in org. phase; MEA concentration = 5.77 kmol/m^3; agitation speed= 1500 rpm; sulfur loading= 1.875 kmol/m^3; temperature = 323 K.

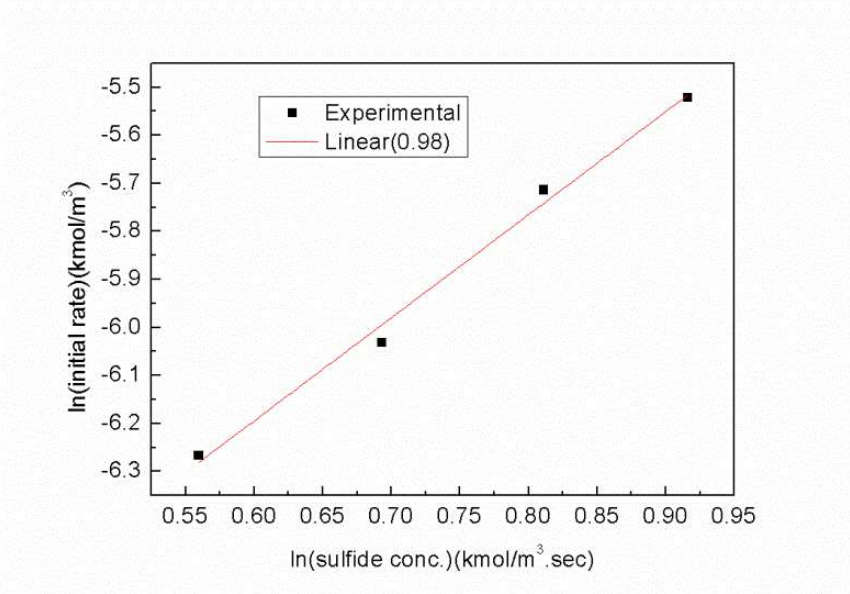


Figure 6.10: Plot of ln(initial rate) vs. ln(conc. of sulfide). All other conditions are same as Fig. 6.9.

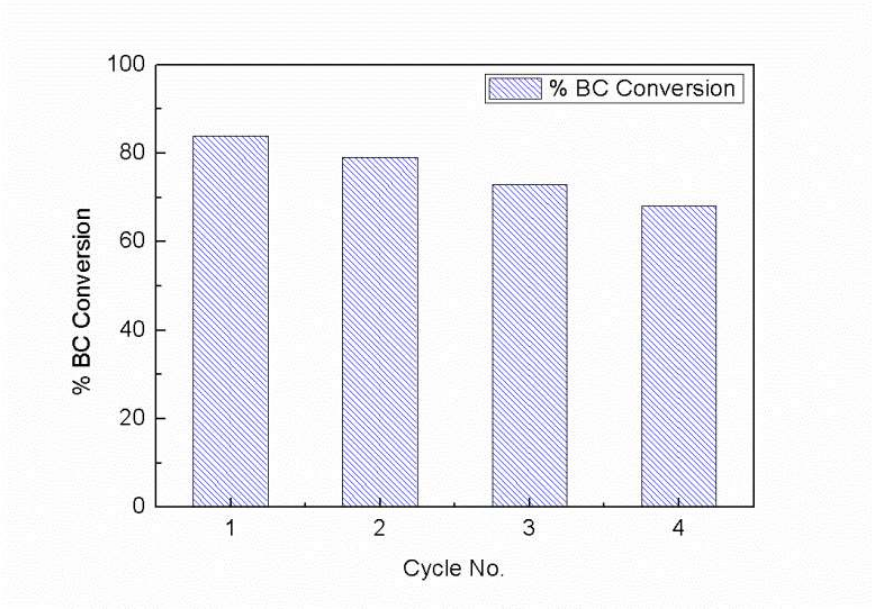


Figure 6.11: Conversion of BC with the cycle number. Operating conditions: volume of aqueous and organic phase = $5.0 \times 10^{-5} m^3$ each; concentration of catalyst = 0.29 kmol/m^3 org phase; concentration of BC = 2.61 kmol/m^3; MEA/H_2S mole ratio = 2.28; sulfur loading= 1.875 kmol/m^3; agitation speed= 1500 rpm; temperature = 323 K.

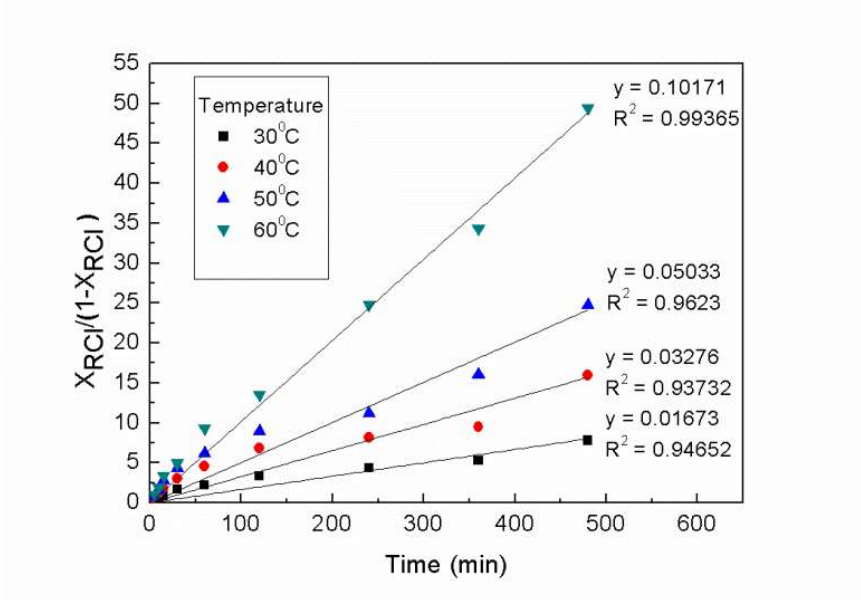


Figure 6.12: Validation of the kinetic model with experimental data at different temperature. volume of organic phase = 5.0 x 10^{-5} m^3, volume of aqueous phase = 5.0 x 10^{-5} m^3; MEA/H_2S mole ratio = 2.28; concentration of catalyst = 0.29 kmol/m^3 org. phase; concentration of toluene= 6.6 kmol/m^3 in org. phase, concentration of BC = 2.6 kmol/m^3in org. phase, sulfide conc. = 2.53 kmol/m^3, stirring speed= 1500 rpm; sulfur loading= 1.875 kmol/m^3.

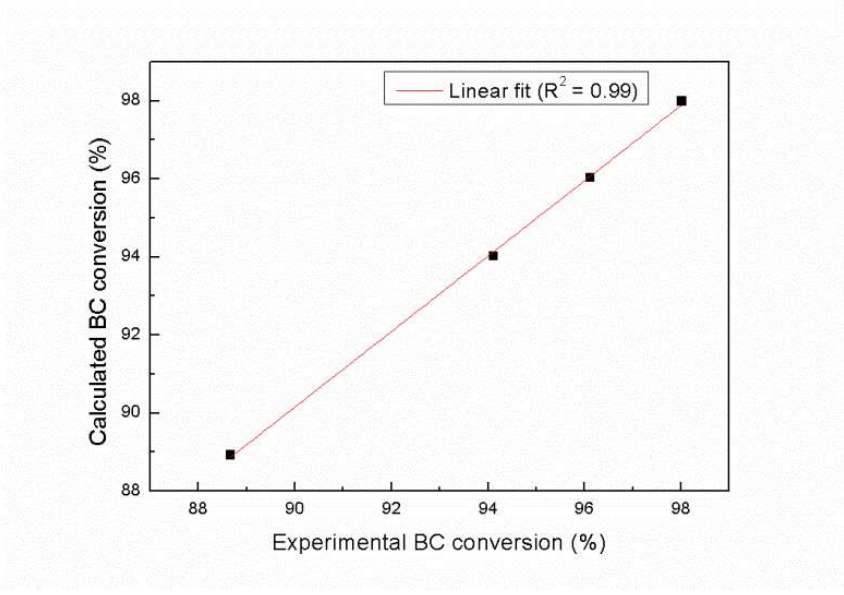


Figure 6.13: Comparison of calculated and experimental BC conversions at 480 min different temperatures and all conditions are as same as Fig. 6.12.

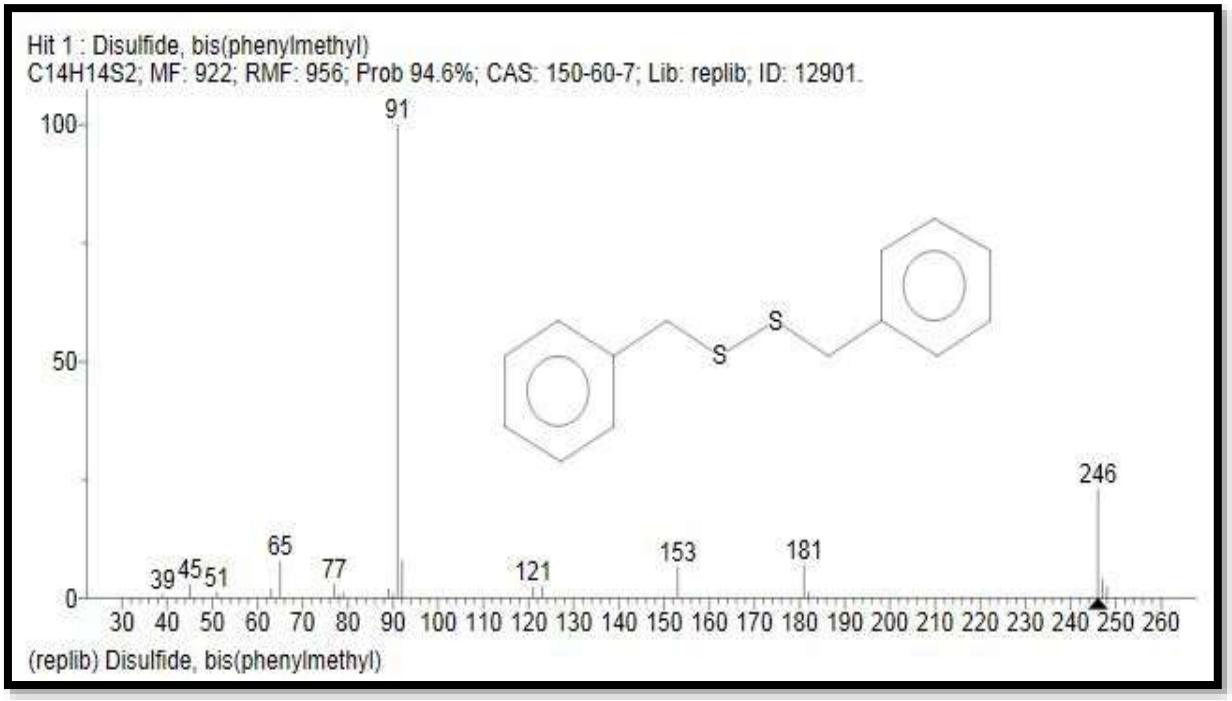


Figure 6.14: MS spectra for DBDS

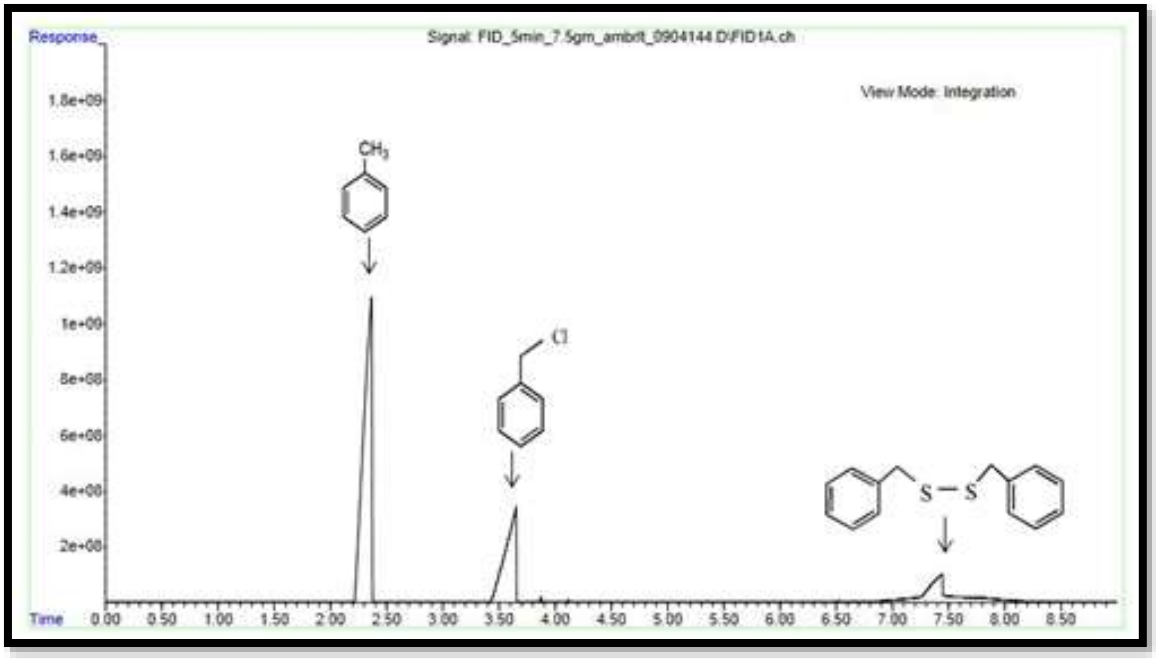


Figure 6.15:GLC chromatogram for DBDS after 5 min of reaction time in presence of Amberlite IR-400

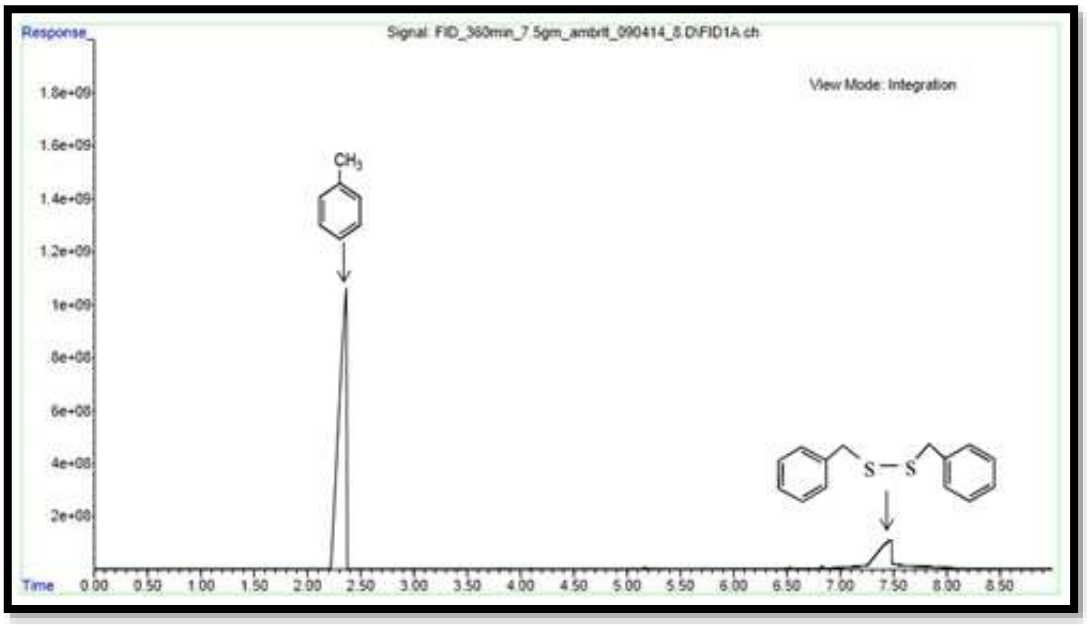


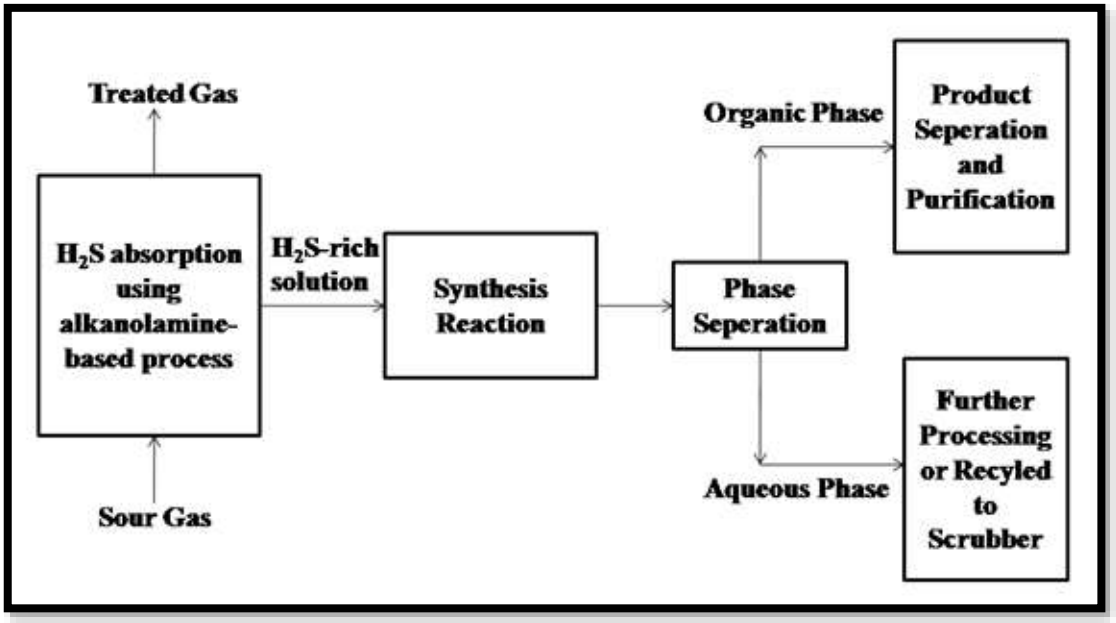
Figure 6.16:GLC chromatogram for DBDS after 480 min of reaction time in presence of Amberlite IR-400

Chapter 7

Conclusion and Future Recommendation

7.1 Introduction

The complete work carried out during the course, was mainly focused on the development of a process to synthesize value-added fine chemicals utilizing H_2S present in the various by-product gas streams. In the present work, H_2S was absorbed in various aqueous alkanolamines. All the experiments were done in a batch reactor, and a detailed experimental, and kinetic study carried out for the synthesis of organosulfur fine chemicals. The schematic flow diagram of the process is represented by Scheme 7.1.



Scheme 7.1

7.1.1 The notable achievements and major conclusions of Chapter 4:

- The synthesis of valuable fine chemical DBS is depicted in Chapter 4. The work has been carried out utilizing H_2S-rich MDEA by reacting it with an organic reactant BC under L-L PTC condition using TBPB as a PTC. The novelty of the work is to utilize industrial amine MDEA for the first time to prepare aqueous sulfiding agent by chemisorption of H_2S and to introduce a phosphonium-based catalyst for the efficient synthesis of DBS.

- MDEA was found to be an effective absorbent for H_2S removal. The average sulfide concentration after a run was found around 2.7 kmol/m^3.
- Experiments were performed with and without catalysts. The rate of reaction, reactant conversion and selectivity of the product was found far better in the presence of a catalyst, so further experiments were performed in the presence of a catalyst. The conversion of reactant reaches to 88% in the presence of a catalyst from 45% in the absence of a catalyst.
- Effect of various process variables, such as stirring speed, catalyst concentration, temperature, sulfide concentration, reactant concentration, MDEA concentration on the conversion of reactant and selectivity of the desired product were studied.
- The proposed mechanism has been successfully explained the course of the reaction. The activation energy for the catalytic reaction has been found to be 70.67 kJ//mol.
- An empirical kinetic model was also developed based on the detailed kinetic study and validated successfully against the experimental data.
- The high DBS yield and selectivity, milder operating conditions and a potentially great substitution to energy-intensive and cost-expensive Claus process makes this method economically and environmentally attractive.

7.1.2 The notable achievements and main findings of Chapter 5:

- In the second reaction system, the same reaction as depicted in Chapter 4 was performed using another PTC, THTDPC, an ionic liquid. The used ILs resulted in a faster reaction (in comparison to TBPB), and higher yield for the product DBS. The selectivity of DBS was found to be 100%.
- Effect of various process variables, such as stirring speed, temperature, catalyst concentration, reactant concentration and sulfide concentration on the conversion of reactant and selectivity of the desired product were studied. The activation

energy for the kinetically controlled reaction system was calculated as 16.88 kJ/mol from the Arrhenius plot.

- A detailed mechanism was proposed to explain the course of the reaction, and a kinetic model was developed based on the mechanism and validated successfully.

7.1.3 The notable achievements and main findings of Chapter 6

- This work based on the synthesis of DBDS, which is having diversified industrial applications. The aim was achievedby the reaction between H_2S-rich MEA with added elemental sulfur powder and BC. The addition of sulfur shifts the equilibrium towards the formation of more disulfide anions and ensures the higher selectivity of DBDS. 100% selectivity of DBDS was observed at 1.875 kmol/m^3 of sulfur loading.

- Amberlite IR 400 (Chloride form) was used as a solid PTC, and the reaction was done under L-L-S PTC condition. As the catalyst was solid and insoluble in either phase, its recovery is easy. Catalyst was recovered and reused four times with slight decrease in the conversion of BC

- It has been found thatat different speeds of agitation, there was no significant change in either the rate of reaction or in the conversion of reactant beyond a stirring speed of 1000 rpm. The reaction was found to be kinetically controlled, and all experiments were done at a stirring speed of 1500 rpm.

- The reaction was found to be approximately first order with respect the concentration of the catalyst, second order with respect to the reactant concentration and second order with respect to the sulfide concentration.

- Effect of various process variables, such as stirring speed, catalyst concentration, temperature, sulfide concentration, reactant concentration, MEA concentration on the conversion of reactant and selectivity of the desired product were studied. The obtained activation energy, for DBDS synthesis, from Arrhenius plot was 56.03 kJ/mol.

- A mathematical model was developed, based on kinetic study and a suitable mechanism was proposed, to account for the calculation of the rate constant. The model was successfully validated against experimental data.

7.2 Future Recommendation

The present work deals with the synthesis of DBS and DBDS utilizing H_2S in the form of H_2S-rich alkanolamines under L-L and L-L-S PTC conditions. The success of the current investigations opens up the door for some other opportunities for research in the following directions:

- The study can also be carried out under solvent free condition then it would be environmental friendly. A few other advantages are, smaller size reactor can be used, the process will become cheaper and handling, and separation of the products will be easier.

- There is a possibility of comparative study among currently used alkanolamines in industries, such as MDEA, MEA, DIPA, and DGA. Also, mixed alkanolamines such as MDEA +DIPA can be used to get the advantage of the most selective removal of H_2S. Physical solvents like polyethylene glycols can be mixed with alkanolamines and used for separation of H_2S.

- Effect of some other parameters on the reactant conversion and product selectivity could be interesting to investigate. The pH of H_2S-rich alkanolamines, the addition of other anions as a co-catalyst (for example NaCl) and adding up alkali (for example NaOH) can give a significant influence on the reaction rate and selectivity towards desired product.

- The present reaction scheme can be applied to synthesize other thioethers and organic disulfides from reactants having active methylene ($-CH_2$) group. Substituted benzyl halide or other heterocyclic having active $-CH_2X$ (X = Cl, Br, I) can be tested for the synthesis of thioethers.

- The reusability plays a significant role from the economic point of view. The other reusable solid PTCs such as 1,3,5-tris(benzyltriethylammonium bromide) benzene

(TBTABB) and polymer-anchored-2-benzyl-2-phenyl-1,3-bis(triethylmethylen ammonium chloride) (PABPBTAC) can also be used.

- The same work can also be carried out under liquid-liquid-liquid (L-L-L) PTC condition by creating a third catalyst-rich phase so that the catalyst-rich phase can be separated and reused again and again.

- The present work was done in two steps; the firststep deals with the making of H_2S-rich alkanolamine solution and the second step deals with the synthesis of organic sulfides and disulfides. The reactions can be tried out in a single step by sending the H_2S gas through a mixture of alkanolamines and the reactants so that simultaneous chemisorption and reaction can take place.

- The present scheme doesn't allow reuse of spent amine solution again. After the reaction, the lean amine solution can be reused to absorb more H_2S and then can be reused as a sulfiding agent again. It can better be achieved in a continuous flow reactor and not in a stirred batch reactor we have used here.

Dissemination

Dissemination

International Journals

1. **Gaurav Singh**, Priya G. Nakade, Dorothy Chetia, Preeti Jha, Ujjal Mondal, Saroj Kumari and Sujit Sen, "Kinetics and mechanism of phase transfer catalyzed synthesis of aromatic thioethers by H_2S-rich methyldiethanolamine'', *J. Ind. Eng. Chjem*. 2016, 37, 190-197.

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3. Ujjal Mondal, Aslam Puthankot, Sujit Sen and **Gaurav Singh**, "Novelties of triphasic phase transfer catalysed Zinin reduction of nitrochlorobenzene by H_2S-laden monoethanolamine", *RSC Advances*. 2015, 2016, 6, 23666 – 23676.

4. Ujjal Mondal, Sujit Sen and **Gaurav Singh**, "Advances in hydrogen sulphide utilisation: phase transfer catalysed selective reduction of nitronaphthalene", *RSC Advances*. 2015, 5, 102942–102952.

5. Preeti Jha, Ujjal Mondal, Devipriya Gogoi, **Gaurav Singh** and Sujit Sen, "Novelties of selective triphasic synthesis of bis-(p-chlorobenzyl) sulfide using hydrogen sulfide and reusable phase transfer catalyst'', *J. Mol. Catal. A Chem*. 2016, 418, 30-40

6. **Gaurav Singh,** Pratik Mishra, Sujit Sen. "Kinetics and mechanism for the synthesis of thioethers using ionic liquids as a phase transfer catalyst". *Under Review.*

7. Pratik Mishra, **Gaurav Singh**, Sujit Sen. "Ionic Liquid Mediated Liquid-Liquid Phase Transfer Catalyzed Synthesis of bis-(2-Phenylethyl) Sulfide with H_2S-rich Methyldiethanolamine under Solvent Free condition", *Under Review*.

8. Sujit Sen, Ujjal Mondal, **Gaurav Singh.** "Dual Optimization in Phase Transfer Catalyzed Synthesis of Dibenzyl Sulfide using Response Surface Methodology (RSM)", *Under Review*.
9. Priya Nakade, Sujit Sen, **Gaurav Singh**, "Tri-liquid Phase Transfer Catalysis: A Review", *Manuscript under preparation.*

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Gaurav Singh, Priya G. Nakade, Preeti Jha, Devipriya Gogoi, Sujit Sen, "Parametric Studies in Synthesis of Aromatic Thioethers using Hydrogen Sulfide under Liquid-Liquid Phase Transfer Catalyst", Indian Chemical Engineering Congress (**CHEMCON-2014**), Punjab University, Chandigarh, India, December 27-30, 2014.

Gaurav Singh, Priya G. Nakade**,** Sujit Sen**,** "Synthesis of Symmetrical Thioethers from Hydrogen Sulfide", Indian Chemical Engineering Congress (**CHEMCON-2013**), ICT Mumbai, India, December 27-30, 2013.

Gaurav Singh, Priya G. Nakade**,** Sujit Sen**,** "Green Routes of Synthesis of Organic Sulphides: A Review", Indian Chemical Engineering Congress (**CHEMCON-2012**), Jalandhar, Punjab, India, December 27-30, 2012.

GAURAV SINGH

Communication

Business Address
Department of Chemical Engineering
National Institute of Technology
Jalandhar – 144011, Punjab, India

Email: gauravsingh.chem@gmail.com
Phone: +91-7809729976 (M)

Home Address
C/O Mr. Pranveer Singh
117/P/341
Kakadeo, Hitkari Nagar,
Kanpur
UP – 208025, India

Education

2012 – Present	**Doctoral Fellow (PhD)** Mentor: **Prof. Sujit Sen** Department of Chemical Engineering. National Institute of Technology Rourkela Title: **"Green Route of Synthesis of Fine Chemicals from Hydrogen Sulfide using Phase Transfer Catalysts"**
2008 – 2010	**Master of Technology (M.Tech.) in Chemical Engineering.** Department of Chemical Engineering. National Institute of Technology, Surat First Class (6.88 CGPA).
2004 – 2008	**Bachelor of Technology (B.Tech.) in Chemical Engineering.** Department of Chemical Engineering. Jawaharlal Darda Institute of Engineering and Technology, Yavatmal, Amaravati University First Class (67.46%).

Personal Dossier

Date of Birth: April 16, 1985
Marital Status: Married
Nationality: Indian